

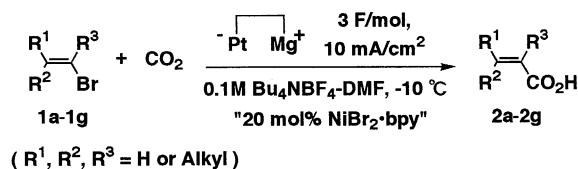
Synthesis of α,β -Unsaturated Carboxylic Acids by Nickel(II)-Catalyzed Electrochemical Carboxylation of Vinyl Bromides

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Electrochemical carboxylation of alkyl-substituted vinyl bromides (**1a-1g**) in the presence of 20 mol% of $\text{NiBr}_2 \cdot \text{bpy}$ under an atmospheric pressure of carbon dioxide with a platinum cathode and a magnesium anode gave the corresponding α,β -unsaturated carboxylic acids (**2a-2g**) in yields of 53-82%.



Scheme 1.

Silvestri^{1,2} and Perichon^{3,4} both reported 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 acids,⁵ allenic acids,⁶ and 3-methylene-4-pentenoic acid⁷ 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 aryl-substituted vinyl bromides to give the corresponding 2-alkenoic acids in high yields.⁸ In the latter paper we showed that a precursor of ibuprofen, 2-(*p*-isobutyl-phenyl)propenoic acid, was readily prepared in a 93% yield.⁸ As part of our continuing studies on the electrochemical synthesis of useful carboxylic acids, we recently carried out the electrochemical carboxylation of alkyl-substituted vinyl bromides. In this paper, we report that the corresponding α,β -unsaturated carboxylic acids are obtained in high yields when the electrochemical carboxylation of alkyl-substituted vinyl bromides is carried out in the presence of Ni(II) complex with a platinum cathode and a magnesium anode under an atmospheric pressure of carbon dioxide. None of aliphatic vinyl halides have been examined in electrochemical carboxylation using a sacrificial anode. The Ni(II)-catalyzed electrochemical reaction of 2-bromo-1-butene in the presence of atmospheric carbon dioxide has only been reported to give 2-ethylpropenoic acid in a 30% yield.⁹

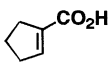
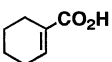
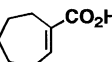
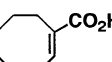
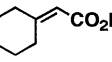
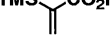
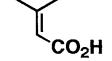
The present electrochemical method is useful for a synthesis of α,β -unsaturated acids since they can readily be prepared in good yields in three steps from the corresponding alkenes. Conventional synthetic methods employ mostly aldehydes or ketones as a starting material.¹⁰

Electrochemical carboxylation of 1-bromocycloalkenes (**1a-1d**)¹¹ under a slow stream of carbon dioxide gas with a platinum cathode and a magnesium anode gave 1-cycloalkene-1-carboxylic acids (**2a-2d**) in yields of 15-43% (Scheme 1). These electrochemical carboxylations were further studied under a variety of conditions in order to obtain higher yields of **2**. We found that the yield of **2a** in the electrochemical carboxylation of **1a** was extremely enhanced to 73% by the addition of 20 mol% nickel(II) bromide-2,2'-bipyridine complex ($\text{NiBr}_2 \cdot \text{bpy}$) to the electrolysis solution. Electrolysis was carried out at 10 mA/cm² in a DMF solution containing 0.1M Bu_4NBF_4 at -10°C under a slow stream

of carbon dioxide gas. An electricity of 3 Faradays per mol of **1a** is required for efficient carboxylation. A one-compartment cell fitted with a platinum plate cathode (2x3 cm²) and a magnesium rod anode (3 mm ϕ) was used for electrolysis.

Electrochemical carboxylation of various vinylic bromides (**1a-1g**) in the presence of 20 mol% of $\text{NiBr}_2 \cdot \text{bpy}$ gave the

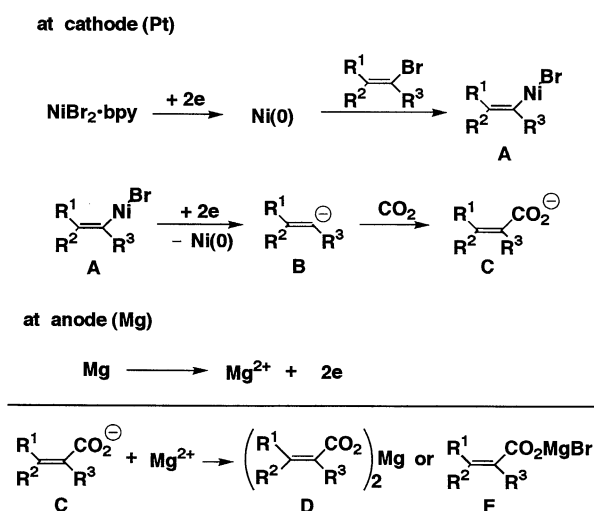
Table 1. Electrochemical carboxylation of alkyl-substituted vinyl bromides ^a

Substrate	Product	Yield of 2 (%) ^b
 1a	 2a	73 (18)
 1b	 2b	58 (15)
 1c	 2c	80 (43)
 1d	 2d	82 (30)
 1e	 2e	58 (14)
 1f	 2f	53 (19)
 1g	 2g	64 (18)

^a Vinylic bromide (3 mmol) in 0.1M Bu_4NBF_4 -DMF (15 ml) was electrolyzed in the presence of 20 mol% of $\text{NiBr}_2 \cdot \text{bpy}$ under an atmospheric carbon dioxide with a Pt cathode and a Mg anode. ^b Isolated yields. Yields in the absence of a Ni complex catalyst are shown in parentheses.

corresponding α,β -unsaturated carboxylic acids (**2a-2g**) in isolated yields of 53-82% (Scheme 1)(Table 1). Similar electrochemical carboxylation of **1a-1g** in the absence of Ni(II) complex gave **2a-2g** in 14-43% yields (Table 1). α,β -Unsaturated carboxylic acids such as **2a-2g**, especially acrylic acid carrying a trimethylsilyl group at the α -position (**2f**), are useful intermediates in organic synthesis.

The probable reaction pathways of the present electrochemical carboxylations are shown in Scheme 2. A two-electron reduction of $\text{NiBr}_2 \cdot \text{bpy}$ gives Ni(0) species, and an oxidative addition of the Ni(0) to vinylic bromide would produce the complex **A**.^{13,14} A two-electron reduction of the complex **A** gives the corresponding vinyl carbanion (**B**), which is trapped by atmospheric carbon dioxide to give the corresponding alkenoate (**C**). At the anode, on the other hand, a dissolution of magnesium metal takes place to give magnesium ion. The magnesium ion readily captures 2-alkenoates (**C**) to give the stable magnesium carboxylate **D** or **E**. Acid treatment of **D** or **E** gives α,β -unsaturated carboxylic acids **2a-2g**. Cyclic voltammetry of **1c** in the presence of $\text{NiBr}_2 \cdot \text{bpy}$ showed the existence of a new reduction peak at ca. -1.5 V vs Ag/AgCl, although the reduction peaks of **1c** and $\text{NiBr}_2 \cdot \text{bpy}$ alone appeared at < -2.6 V and -1.25 V, respectively. Detailed study on the reaction pathways of the present electrochemical carboxylation is now in progress.



Scheme 2.

Electrochemical carboxylation of vinylic bromides **1** gave low yields of products **2** when the electrolysis was carried out in the absence of Ni(II) complex. It is probably due to an ineffective reduction of **1** which has negative reduction potential (< -2.6 V vs Ag/AgCl). Apparent reduction potentials of **1** were moved to more positive ones (-1.5V) by the addition of the Ni(II) complex, which probably resulted in increased yields of **2**.

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References and Notes

- G. Silvetsri, S. Gambino, G. Filardo, and A. Gulotta, *Angew. Chem. Int. Ed. Engl.*, **23**, 979 (1984).
- G. Silvetsri, S. Gambino, and G. Filardo, *Acta Chem. Scand.*, **45**, 987 (1991).
- O. Sock, M. Troupel, and J. Perichon, *Tetrahedron Lett.*, **26**, 1509 (1985).
- J. Chaussard, J. C. Folest, J. Y. Nedelec, J. Perichon, and S. Sibille, and M. Troupel, *Synthesis*, 369 (1990).
- M. Tokuda, T. Kabuki, Y. Katoh, and H. Sugimoto, *Tetrahedron Lett.*, **36**, 3345 (1995).
- M. Tokuda, T. Kabuki, and H. Sugimoto, *DENKI KAGAKU*, **62**, 1144 (1994).
- M. Tokuda, A. Yoshikawa, H. Sugimoto, and H. Senboku, *SYNTHESIS*, in press (1997).
- H. Kamekawa, H. Senboku, and M. Tokuda, *Electrochimica Acta*, **42**, 2117 (1997).
- L. Garnier, Y. Rollin, and J. Perichon, *J. Organomet. Chem.*, **367**, 347 (1989).
- E. W. Colvin, in "Comprehensive Organic Chemistry," ed by D. Barton and W. D. Ollis, Pergamon, Oxford (1979), Vol.2, part 9, p.617.
- 1-Bromocycloalkenes **1a**, **1b**, **1c**, and **1d** were prepared from the corresponding cycloalkenes by the bromination-dehydrobromination procedure. Bromomethylenecyclohexene (**1e**) was prepared according to the published method.¹²
- B. M. Trost, J. Dumas, and M. Villa, *J. Am. Chem. Soc.*, **114**, 9836 (1992).
- J. F. Fauvarque, A. Jutand, and M. Francois, *J. Appl. Electrochem.*, **18**, 109 (1988).
- S. Durandetti, S. Sibille, and J. Perichon, *J. Org. Chem.*, **54**, 2198 (1989).