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

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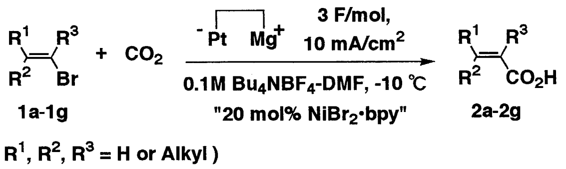
Electrochemical carboxylation of alkyl-substituted vinyl bromides (**1a**-**1g**) in the presence of 20 mol% of $NiBr_2$•bpy under an atmospheric pressure of carbon dioxide with a platinum cathode and a magnesium anode gave the corresponding α,β-unsaturated carboxylic acids (**2a**-**2g**) in yields of 53-82%.

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 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 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*-isobutylphenyl)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]

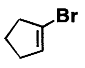
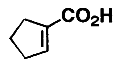
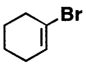
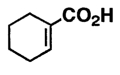
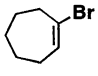
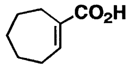
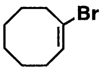
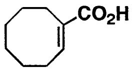
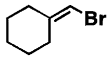
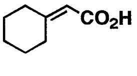
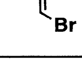
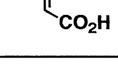
Electrochemical carboxylation of 1-bromocycloalkenes (**1a**-**1d**)[11] under a slow stream of carbon dioxide gas with a platinum cathode and a magnesium anode gave 1-cycloalkene-1-carboxylic acids (**2a**-**2d**) in yields of 15-43% (Scheme 1). These electrochemical carboxylations were further studied 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 ($NiBr_2$•bpy) to the electrolysis solution. Electrolysis was carried out at 10 mA/cm^2 in a DMF solution containing 0.1M Bu_4NBF_4 at -10 ℃ 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 cm^2) and a magnesium rod anode (3 mmφ) was used for electrolysis.



Scheme 1.

Electrochemical carboxylation of various vinylic bromides (**1a**-**1g**) in the presence of 20 mol% of $NiBr_2$•bpy gave the

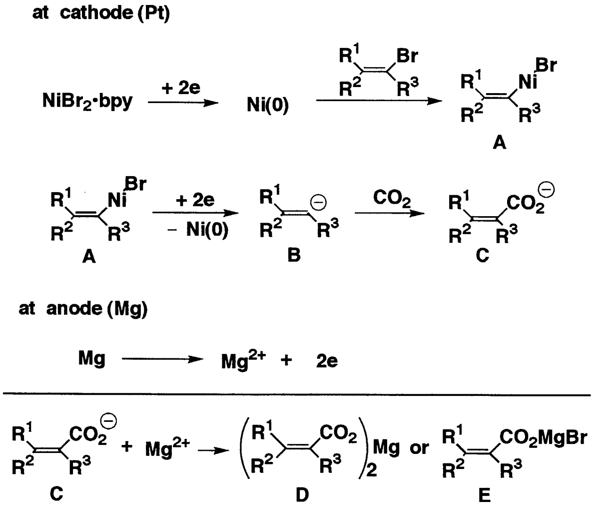
Table 1. Electrochemical carboxylation of alkyl-substituted vinyl bromides [a]

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 $NiBr_2$•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 $NiBr_2$•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 $NiBr_2$•bpy showed the existence of a new reduction peak at ca. -1.5 V *vs* Ag/AgCl, although the reduction peaks of **1c** and $NiBr_2$•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 petentials 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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