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Stereospecific Electrochemical Carboxylation of β -Bromostyrene by Use of Nickel(II) Catalyst

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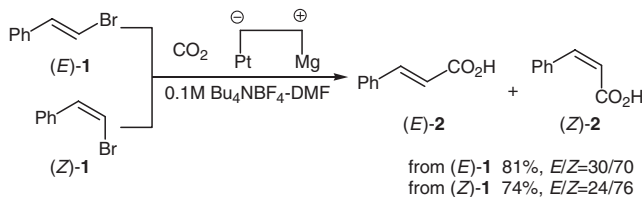
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Electrochemical carboxylation of (*E*)- and (*Z*)- β -bromostyrenes (**1**) under an atmospheric pressure of carbon dioxide with a platinum cathode and a magnesium anode in the presence of 20 mol % of $\text{NiBr}_2 \cdot \text{bpy}$ proceeded with retention of stereochemistry to give the corresponding (*E*)- or (*Z*)-cinnamic acids (**2**). The stereochemical outcome of nickel(II)-catalyzed electrochemical carboxylations was discussed by comparison with predominant formation of a (*Z*)-isomer from either (*E*)- or (*Z*)- β -bromostyrenes.

Electrochemical carboxylation is one of the most useful methods for the fixation of carbon dioxide to organic molecules because it is a clean and environmentally benign process. It takes place efficiently even in an atmospheric pressure of CO_2 under neutral and mild conditions to give carboxylic acids in high yields when a reactive-metal such as magnesium or aluminum is used as a sacrificial anode in the electrolysis.¹ We have already reported that electrochemical carboxylation of vinyl halides and vinyl triflates gave the corresponding carboxylic acids in high yields.² In 1996, we found that thermodynamically less-stable (*Z*)-cinnamic acids ((*Z*)-**2**) were preferentially produced from either (*E*)- or (*Z*)- β -bromostyrene ((*E*)-**1** or (*Z*)-**1**) in the electrochemical carboxylations.³ Electrochemical carboxylation of (*E*)-**1** gave a 30/70 mixture of (*E*)-**2** and (*Z*)-**2**, whereas that of (*Z*)-**1** also gave a 24/76 mixture of (*E*)-**2** and (*Z*)-**2** (Scheme 1).



Scheme 1.

As one of our continuing studies on electrochemical carboxylation, we attempt to develop a novel route for the stereoselective electrochemical carboxylation of (*E*)-**1** and (*Z*)-**1** by use of nickel(II) catalyst. In this paper, we report our results concerning stereoselective electrochemical carboxylation and mechanistic aspects of this reaction.

We first examined the electrochemical carboxylation of (*E*)-**1** under various conditions. The results are summarized in Table 1. Various conditions were examined to optimize the yield and stereoselectivity. It was found that electrochemical carboxylation of (*E*)-**1** in the presence of 20 mol % of nickel(II) bromide-2,2'-bipyridine complex ($\text{NiBr}_2 \cdot \text{bpy}$), at -10°C and 5 mA/cm^2 of constant current with an electricity of 3 Faradays per mol of (*E*)-**1** gave the corresponding acid **2** (*E/Z* = 99/1)

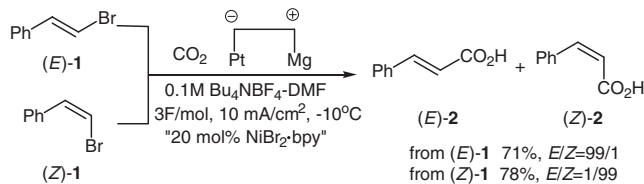
Table 1. Electrochemical carboxylation of (*E*)- β -bromostyrene ((*E*)-**1**) under various conditions^a

Entry	Catalyst $\text{NiBr}_2 \cdot \text{bpy}$	Temperature $^\circ\text{C}$	Current density $/\text{mA cm}^{-2}$	Electricity $/\text{F mol}^{-1}$	Yield $\%^b$	Isomer ratio <i>E/Z</i> ^c
1	—	5	10	3	81	30/70
2	—	-10	10	3	61	21/79
3	10 mol %	-10	10	3	66	78/22
4	20 mol %	-10	10	3	65	88/12
5	20 mol %	-10	15	3	47	67/33
6	20 mol %	-10	5	3	71	99/1
7	20 mol %	20	10	3	72	91/9
8	20 mol %	-10	5	4.5	76	77/23

^a(*E*)- β -bromostyrene (3 mmol) in 0.1 M 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. ^bIsolated yields. ^cIsomer ratios were determined by $^1\text{H NMR}$.

with retention of its stereochemistry in a 71% yield (Table 1, Entry 6).

Similar nickel-catalyzed electrochemical carboxylation of (*Z*)-**1** under the same condition as that of (*E*)-**1** gave the corresponding acid **2** (*E/Z* = 1/99) in a 78% yield (Scheme 2).⁴ The use of an aluminum or zinc anode, instead of magnesium anode, in the electrochemical carboxylation of (*E*)-**1** resulted in a decreased yield and stereochemistry of the acid **2**. Electrochemical carboxylation of (*E*)-**1** in the presence of 20 mol % of $\text{NiBr}_2 \cdot \text{bpy}$, using a platinum cathode and an aluminum anode gave a 76/24 mixture of (*E*)-**2** and (*Z*)-**2** only in a 45% yield. Additionally, electrochemical carboxylation of (*E*)-**1** using a zinc anode gave a mixture of acid **2** (*E/Z* = 73/27) in only a 9% yield. These results show that a magnesium anode plays an important role in efficient electrochemical carboxylation and its stereochemistry. It was also found that palladium catalyst such as $\text{Pd}(\text{PPh}_3)_4$, $\text{PdCl}_2(\text{PPh}_3)_2$ were not effective in this reaction.

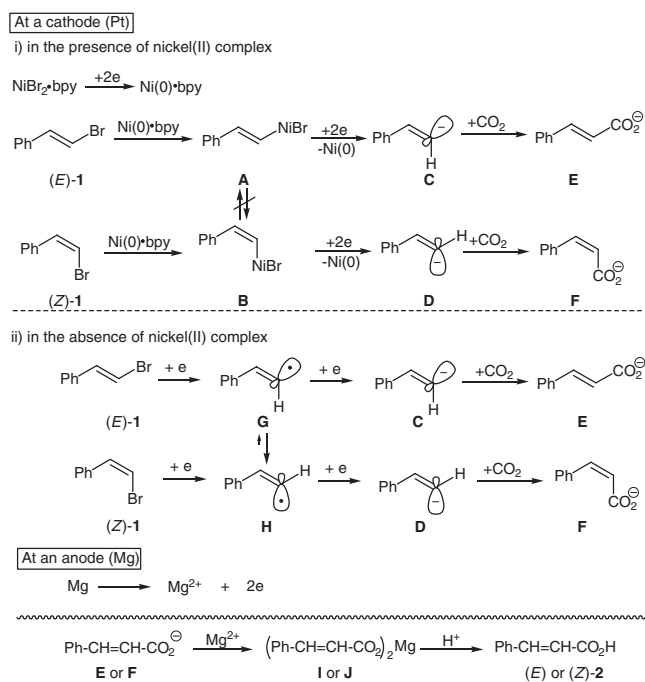


Scheme 2.

The present electrochemical method is useful for the synthesis of substituted (*E*)- or (*Z*)-cinnamic acids since the starting (*E*)- or (*Z*)-vinyl bromides can readily be prepared in high yields.⁵ The electrochemical carboxylation of (*Z*)-vinyl bromides with CO_2 has especially been proposed as a useful proce-

dures for the production of (Z)-cinnamic acids which are difficult to prepare by conventional method,^{6a} even though the conversion of (E)-cinnamic acids to its (Z)-isomer has been reported.^{6b}

The probable reaction pathways of the present electrochemical carboxylation are shown in Scheme 3. At the cathode, in the presence of nickel catalyst, a two-electron reduction of $\text{NiBr}_2 \cdot \text{bpy}$ gives $\text{Ni}(0)$ species, and an oxidative addition of the $\text{Ni}(0)$ to (E)- or (Z)-**1** would produce the intermediate **A** or **B**, isomerization could not occur between **A** and **B** at this stage. A two-electron reduction of **A** or **B** gives the corresponding vinyl carbanion (**C** or **D**), which is trapped by atmospheric carbon dioxide to give the corresponding alkenoate (**E** or **F**). 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 (**E** or **F**) to give the stable magnesium carboxylate **I** or **J**. Acid treatment of **I** or **J** gives (E)-**2** or (Z)-**2**. Cyclic voltammetry of (E)-**1** and (Z)-**1** in the presence of $\text{NiBr}_2 \cdot \text{bpy}$ showed the existence of an additional reduction peak at ca. -1.98 and -1.97 V vs Ag/AgCl , respectively, while the reduction peaks of (E)-**1**, (Z)-**1** and $\text{NiBr}_2 \cdot \text{bpy}$ alone appeared at -2.59 , -2.62 , and -1.53 V, respectively.⁷ These results suggest that in the presence of $\text{NiBr}_2 \cdot \text{bpy}$, a direct two-electron reduction of intermediate **A** or **B** may take place preferentially over a one-electron reduction giving an equilibration between two (E)- and (Z)-vinyl radical.



Scheme 3.

In the absence of nickel catalyst, a one-electron reduction of (E)- or (Z)-**1** gives the corresponding vinyl radical **G** or **H**, respectively (Scheme 3). In an equilibration between vinyl radicals **G** and **H**, the radical **H** would gain an advantage over radical **G** due to some interaction of a magnesium ion with a phenyl group and a radical center. When a platinum anode, instead of a magnesium anode, was used in the electrochemical carboxylation of (E)-**1**, (E)-**2** was predominantly produced. This result indicates that a magnesium ion, formed by dissolution of a magne-

sium anode in electrolysis, plays an important role in the (Z)-selectivity of electrochemical carboxylation of vinyl bromides. In order to find a further evidence of this prospect, we investigated the electrochemical carboxylation of (Z)-1-bromo-3-cyclohexylethylene ((Z)-**3**) in the absence of nickel catalyst, much to our delight, a 51/49 mixture of (E)- and (Z)-3-cyclohexylpropenoic acid ((E)- and (Z)-**4**) was obtained in a 23% yield. Because of an absence of π -electron in cyclohexyl group, stability of the two vinyl radicals is not so different, hence electrochemical carboxylation of (Z)-**3** gave the (E)- and (Z)-**4** in almost same ratio. These results showed that both π -electron of phenyl group and magnesium ion are essential in regulation of the stereoselectivity of electrochemical carboxylation of vinyl bromides.

In summary, we have developed a novel route for the stereoselective electrochemical carboxylation of β -bromostyrene by use of nickel(II) catalyst. The stereochemical mechanistic aspects of nickel(II)-catalyzed electrochemical carboxylations are discussed by comparison with predominant formation of a (Z)-isomer from either (E)- or (Z)- β -bromostyrenes.

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References and Notes

- a) G. Silvestri, S. Gambino, G. Filardo, and A. Gulotta, *Angew. Chem., Int. Ed. Engl.*, **23**, 979 (1984). b) O. Sock, M. Troupel, and J. Périchon, *Tetrahedron Lett.*, **26**, 1509 (1985).
- a) H. Kamekawa, H. Kudoh, H. Senboku, and M. Tokuda, *Chem. Lett.*, **1997**, 917. b) H. Kamekawa, H. Senboku, and M. Tokuda, *Tetrahedron Lett.*, **39**, 1591 (1998). c) H. Senboku, H. Kanaya, Y. Fujimura, and M. Tokuda, *J. Electroanal. Chem.*, **507**, 82 (2001).
- H. Kamekawa, H. Senboku, and M. Tokuda, *Electrochim. Acta*, **42**, 2117 (1997).
- Typical procedure for the nickel(II)-catalyst electrochemical carboxylation of β -bromostyrene is described in the followings: A mixture of (E)- β -bromostyrene ((E)-**1**, 3 mmol) and $\text{NiBr}_2 \cdot \text{bpy}$ (0.6 mmol) and Bu_4NBF_4 (1.5 mmol) in 15 mL of DMF was added into a one-compartment cell equipped with a platinum plate cathode ($2 \times 3 \text{ cm}^2$) and a magnesium rod anode ($3 \text{ mm}\phi$). The mixture was electrolyzed at -10°C at $5 \text{ mA}/\text{cm}^2$ of constant current under a slow stream of carbon dioxide gas until an electricity of 3 Faradays per mol of (E)-**1** was passed. The electrolyzed solution was poured into 2N HCl and extracted with diethyl ether ($3 \times 50 \text{ mL}$). After the organic layer was washed with water ($4 \times 50 \text{ mL}$), it was extracted by saturated sodium hydrogen carbonate ($3 \times 50 \text{ mL}$). The aqueous layer was again acidified with 2N HCl and extracted with diethyl ether ($3 \times 50 \text{ mL}$). The organic layer was washed with brine and dried over MgSO_4 . Filtration and evaporation of the solvent afforded cinnamic acid **2** (E/Z = 99/1) in 71% yield. Mp $133\text{--}134^\circ\text{C}$; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 6.46 (1H, d, $J = 16.1 \text{ Hz}$), 7.39–7.44 (3H, m), 7.52–7.57 (2H, m), 7.80 (1H, d, $J = 16.1 \text{ Hz}$); $^{13}\text{C NMR}$ (67.5 MHz, CDCl_3) δ 117.30, 128.35, 128.93, 130.72, 133.98, 147.09, 172.66.
- a) C. Kuang, H. Senboku, and M. Tokuda, *Synlett*, **2000**, 1439. b) C. Kuang, H. Senboku, and M. Tokuda, *Tetrahedron Lett.*, **42**, 3893 (2001). c) C. Kuang, H. Senboku, and M. Tokuda, *Tetrahedron*, **58**, 1491 (2002). d) C. Kuang, H. Senboku, and M. Tokuda, *Tetrahedron*, **61**, 637 (2005), and references cited therein.
- a) M. B. Hocking, *Can. J. Chem.*, **47**, 4567 (1969). b) V. Galamb and H. Alper, *Tetrahedron Lett.*, **24**, 2965 (1983).
- Reduction peak potentials of (E)- and (Z)- β -bromostyrene and $\text{NiBr}_2 \cdot \text{bpy}$ were determined by cyclic voltammetry of 2 mM substrates in 0.1 M Bu_4BF_4 -DMF with a gold disk electrode ($1.6 \text{ mm}\phi$) at the scan rate of 0.1 V/s.