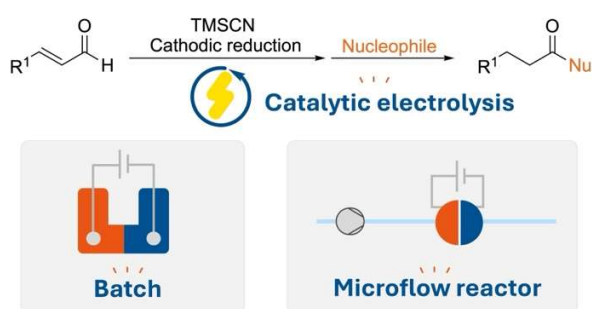


Transformation of α,β -Unsaturated Aldehydes with a Small Amount of Electricity: Cyanosilylation, Isomerization, and Nucleophilic Addition

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Supporting Information Placeholder



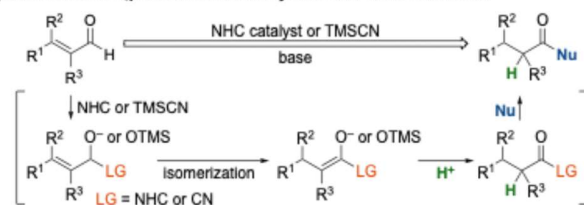
ABSTRACT: An electrochemical method has been developed to convert α,β -unsaturated aldehydes to carboxylic acid derivatives via cyanosilylation, isomerization, and nucleophilic addition. This reaction is more sustainable than the usual electrochemical organic reaction because this reaction proceeds catalytically with active species generated by a very small amount of electricity. Furthermore, scale-up synthesis with a flow reactor has been achieved.

Redox economy is the strategic minimization of redox steps in organic chemical synthesis to increase efficiency and is considered an important concept in multi-step organic chemistry.¹ Various reactions that use umpolung by *N*-heterocyclic carbene (NHC) catalysts² have been investigated to fulfill this requirement. For example, in 2005, Scheidt reported a transformation of α,β -unsaturated aldehydes into esters and amides catalyzed by NHCs (Scheme 1a).³ The reaction between α,β -unsaturated aldehydes and NHCs gave homoenolate equivalents, which undergo nucleophilic substitution to afford esters and amides.⁴ In this reaction, an aldehyde is oxidized to an ester and amide in conjunction with the reduction of a neighboring double bond through an intramolecular redox-transfer process. Since aldehyde can be converted to carboxylic acid derivatives without any external oxidants, this reaction seems to be desirable from the viewpoint of redox economy.¹ Hayashi reported that trimethylsilyl cyanide (TMSCN) can also be used a similar redox-neutral transformation of α,β -unsaturated aldehydes to saturated esters under basic conditions.⁵ Fukuyama further investigated the scope of this reaction and applied it to terpene synthesis.⁶

Recently, Yuan and we independently developed the electrochemical cyanosilylation of carbonyl compounds promoted by cathodic reduction.⁷ The reaction went to completion with a catalytic amount of electricity,⁸ and various carbonyl compounds gave the corresponding cyanohydrins.

During our examination of the substrate scope, we could not achieve reproducibility of cyanosilylation when cinnamaldehyde was used as a starting material. We consider that the cyanohydrin would undergo isomerization to form silyl enol ethers, which act as nucleophiles. Against this background, we started research on the development of a method for redox transformation of α,β -unsaturated aldehydes with a small amount of electricity to form saturated esters and amides (Scheme 1b). The present protocol is very simple and environmentally friendly without chemical reagents. Since there have been few reported studies on the reaction mechanism,^{5,6} we have also conducted a detailed study, including confirmation of the reaction intermediates by considering the NMR spectrum.

a) Conversion of α,β -unsaturated aldehydes under basic conditions



b) This work (electrochemical approach)

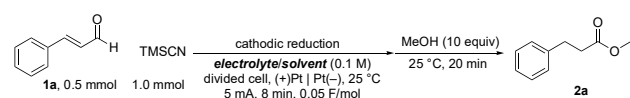


Scheme 1. Transformation of α,β -Unsaturated Aldehydes to Carboxylic Acid Derivatives

First, we performed the cathodic reduction of a mixture of cinnamaldehyde (**1a**) and TMSCN followed by the addition of methanol to afford corresponding methyl ester **2a** using various solvent–electrolyte combinations (Table 1). The chosen solvent greatly affected the progress of isomerization (entries 1–5), and CH_2Cl_2 , which was used as a solvent for our electrochemical cyanosilylation of carbonyl compounds,^{7b} did not afford methyl ester in good yield (entry 1). When other solvents, such as CH_3CN , DMSO and DMF, were used, the methyl ester was obtained in low yields (entries 2–4). In contrast, THF dramatically improved the yield (entry 5). The lower acceptor number of THF would cause smaller interactions with the anionic species generated through cathodic reduction and resulted in a good yield.⁹ Next, we investigated the effects of the supporting electrolytes (entries 5–7). When the reactions were performed with Bu_4NBF_4 , Bu_4NClO_4 , and Bu_4NPF_6 as supporting electrolytes, the yields were almost identical, with Bu_4NPF_6 giving the best yield. Based on the results of the experiments described above, we determined that a THF– Bu_4NPF_6 system was a good combination for the electrochemical cyanosilylation, isomerization, and nucleophilic substitution sequence.

Next, the electrochemical parameters were examined (Table 2). While a slight decrease of the yield was observed with 1 mA of current (entry 1), an increase in current to 10 mA gave better results (entry 3). When only 0.025 F/mol of electricity was applied, the yield was low, and the starting material and cyanohydrin trimethylsilyl ether remained unreacted (entry 4). The highest yield was obtained at 0.05 F/mol (entry 3), and the yield of the target product decreased with an increase in the total amount of electricity (entries 5–8). When 0.05 F/mol of electricity was applied, only 5 mol% of electron was introduced to the reaction mixture. These results indicated that an electrochemical cyanosilylation and isomerization sequence could go to completion with a catalytic amount of electricity, and a Faraday efficiency of more than 1600% was achieved.

Table 1. Effect of the Solvent and Electrolyte



entry	solvent	supporting electrolyte	yield (%) ^a
1	CH_2Cl_2	Bu_4NPF_6	10
2	CH_3CN	Bu_4NPF_6	50
3	DMSO	Bu_4NPF_6	25
4	DMF	Bu_4NPF_6	67
5	THF	Bu_4NPF_6	83
6	THF	Bu_4NBF_4	75
7	THF	Bu_4NClO_4	80

^a The yields were determined by ^1H NMR analysis using ethylene carbonate as an internal standard.

Table 2. Effect of the Current and Total Amount of Electricity

entry	current (mA)	the total amount of electricity (F/mol)	yield (%) ^a
1	1	0.05	74
2	5	0.05	83
3	10	0.05	91
4	10	0.025	78
5	10	0.1	85
6	10	0.25	72
7	10	0.5	52
8	10	1	25
9	No electricity		N.R. ^b

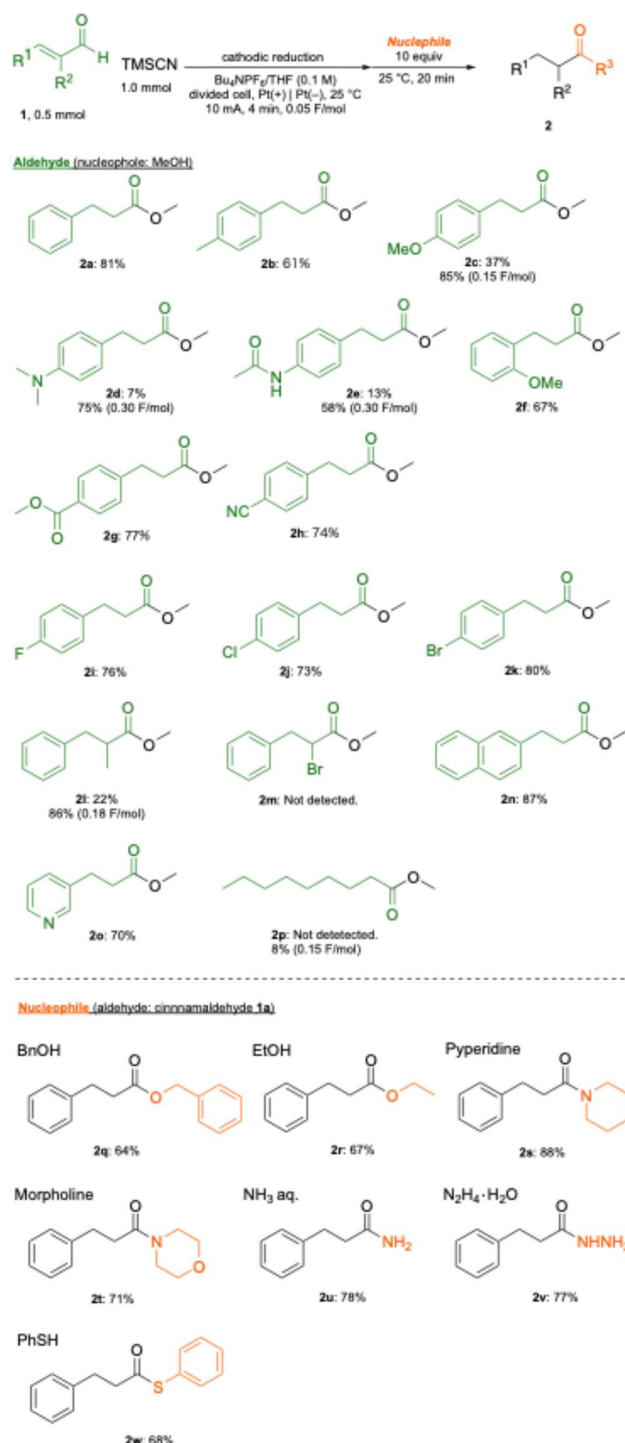
^a The yields were determined by ^1H NMR analysis using ethylene carbonate as an internal standard. ^b No reaction.

With the optimized reaction conditions in hand, we investigated the reactivity of various α,β -unsaturated aldehydes under the optimized conditions (Scheme 2). Low yields were recorded with electron-donating groups, and unreacted starting materials were recovered (**2c–e**). To consume the starting material completely, 0.15 F/mol was applied to these electron-donating substrates (**2c**). As a result, the yield increased to 85%. The yields of the other substrates also improved with an increase in the total amount of electricity (**2d**, **2e**). The lower reactivities of these compounds would be derived from the higher electron density, which results in less electrophilicity, at the carbonyl group. When a substrate with a methoxy group at the ortho position was used, the desired product was obtained in 67% yield (**2f**). On the other hand, substrates functionalized with electron-withdrawing groups gave good yields (**2g–k**). Although the target reaction proceeded with a substrate having a methyl group at the α -position of the carbonyl group, the yield was low (**2l**). It would be difficult for cyanosilylation to proceed due to steric hindrance, and the starting material was recovered. The yield was greatly improved by increasing the total amount of electricity. The electron-withdrawing nature of the bromo group at the α -position of the carbonyl group would disturb the isomerization, and only the cyanohydrin trimethylsilyl ether, which is a possible intermediate (vide infra), was obtained in 71% yield (**2m**). Substrates containing naphthalene or pyridine as aromatic moieties gave good yields (**2n**, **2o**). The reaction was less likely to proceed with a substrate without an aromatic moiety and the yield was only 8% when 0.15 F/mol of electricity was applied (**2p**).

We examined the reactions of various nucleophiles. The reaction gave the desired products in good yields with some other alcohols, such as benzyl alcohol and ethanol (**2q**, **2r**).

Amines and thiols also gave good yields, and the corresponding amide and thioester were obtained (**2s–w**).

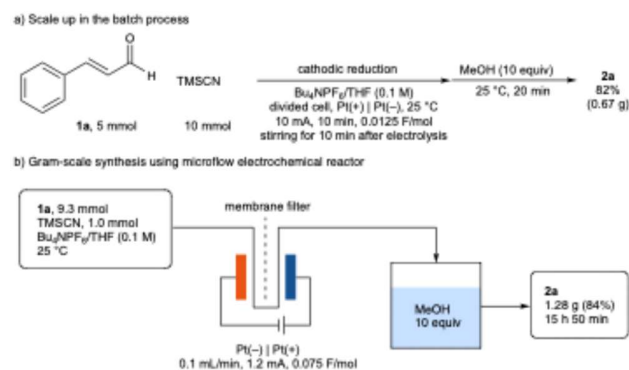
Scheme 2. Substrate Scopes and Limitation of the Reaction



Additionally, to scale up the reaction under batch conditions, the substrate concentration of **1a** was increased ten-fold from the standard conditions, using 5 mmol of starting material (Scheme 3a). To complete the isomerization reaction, a stirring time of 10 minutes was required after electrolysis. Despite the use of a very small amount of electricity (0.0125 F/mol), the reaction proceeded to give the product

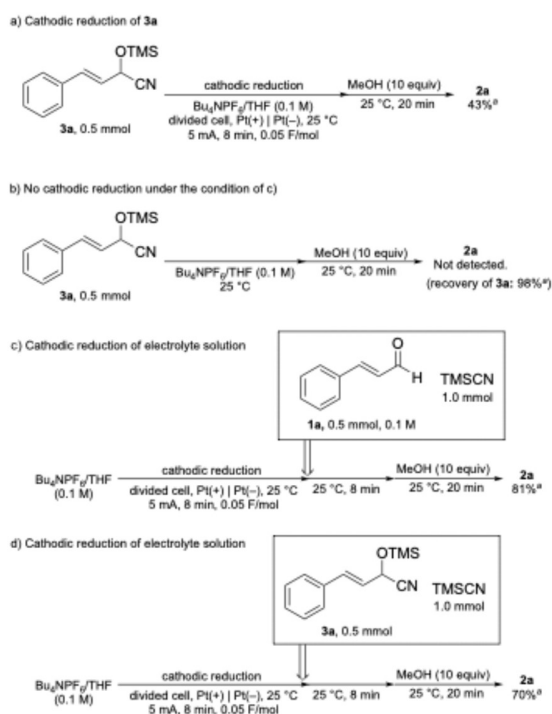
in 82% yield, even under these modified conditions. Furthermore, gram-scale synthesis was carried out using a micro-flow electrochemical reactor (Scheme 3b).¹⁰ The solution of **1a**, TMSCN, and Bu₄NBF₄ in THF was pumped to the microflow electrochemical reactor, and constant current was applied. The solution was introduced to a cathodic chamber, and the cathodic solution was transferred to an anodic chamber. The electrolyzed solution was added to methanol to afford methyl ester (**2a**). After 93 mL of solution was flowed over 15 h 50 min, 1.28 g of **2a** was obtained in 84% yield.

Scheme 3. Scale-up synthesis in the batch and flow process



To investigate the reaction mechanism, several control experiments were performed. First, the cathodic reduction of cyanohydrin trimethylsilyl ether **3a** and the subsequent addition of methanol gave methyl ester **2a** in 43% yield (Scheme 4a).¹¹ When cyanohydrin trimethylsilyl ether **3a** was not reduced, isomerization did not proceed even if methanol was added after stirring with the electrolyte (Scheme 4b). These results indicate that cyanohydrin trimethylsilyl ether **3a** is an intermediate. It was found that electricity is also required for the reaction after cyanohydrin trimethylsilyl ether **3a** is formed. Moreover, we performed the pre-cathodic reduction of the electrolyte solution without both cinnamaldehyde (**1a**) and TMSCN, and then cinnamaldehyde (**1a**) and TMSCN were added into the reduced solution. After the mixture was stirred for 8 min, the addition of methanol allowed the generation of methyl ester **2a** in 81% yield (Scheme 4c). Also, when cyanohydrin trimethylsilyl ether **3a** and TMSCN were added into the reduced solution instead of cinnamaldehyde (**1a**) and TMSCN, methyl ester **2a** was obtained in 70% yield (Scheme 4d). These results indicate that the electro-generated base (EGB)¹² can promote both cyanosilylation and isomerization¹³ although a mechanism involving direct electrolysis could not be completely ruled out.

Scheme 4. Control Experiments



^a The yields were determined by ¹H NMR analysis using ethylene carbonate as an internal standard.

Next, the direct NMR analysis of the reaction solution was carried out to analyze the intermediates (Figure 1).¹⁴ When electricity was applied to the reaction mixture at 5 mA for 2 min (0.0125 F/mol), the formation of cyanohydrin trimethylsilyl ether **3a** was observed at 6.83, 6.31, and 5.32 ppm. Signals at 5.78 and 3.49 ppm indicate the *Z* isomer of silyl enol ether **4a**, and 5.86 and 3.54 ppm signals indicate its *E* isomer.¹⁵ The signals at 2.91 and 2.50 ppm indicate the formation of acyl cyanide **5a**, which would be formed by the reaction of silyl enol ether **4a** with a residual amount of water. After further electrolysis for 8 min (0.05 F/mol), cyanohydrin trimethylsilyl ether **3a** completely disappeared, and only silyl enol ether **4a** and acyl cyanide **5a** were observed. Direct NMR analysis suggested that cyanohydrin trimethylsilyl ether **3a** is relatively unstable and readily isomerizes to silyl enol ether **4a** under cathodic reduction conditions.¹⁶

According to the results of control experiments, direct NMR analysis and our previous report,^{7b} we propose the reaction mechanism shown in Scheme 5. First, cathodic reduction initiates the cyanosilylation of cinnamaldehyde (**1a**), affording cyanohydrin trimethylsilyl ether **3a**. Although it cannot be completely ruled out that this reaction proceeds in part via an electro-generated base, our previous report^{7b}—particularly the results of DFT calculations—indicates that the reaction proceeds via an electron-catalyzed pathway. Without subjecting compound **3a** to electroreductive conditions, isomerization does not occur (Scheme 4a and b). Furthermore, since the reduction potential of TMSCN is more positive than that of **3a** (see the Supporting Information), it is unlikely that **3a** would be reduced under conditions where both TMSCN and **3a** are present. Based on these results, the EGB promotes isomerization to form silyl enol ether **4a**. As mentioned above, the NMR experiments

support this isomerization and confirm the formation of a mixture of *E*- and *Z*-isomers of silyl enol ether **4a** (Figure 1). Upon addition of methanol, protonation of **4a** yields acyl cyanide **5a**, which subsequently reacts with methoxide to produce methyl ester **2a**.

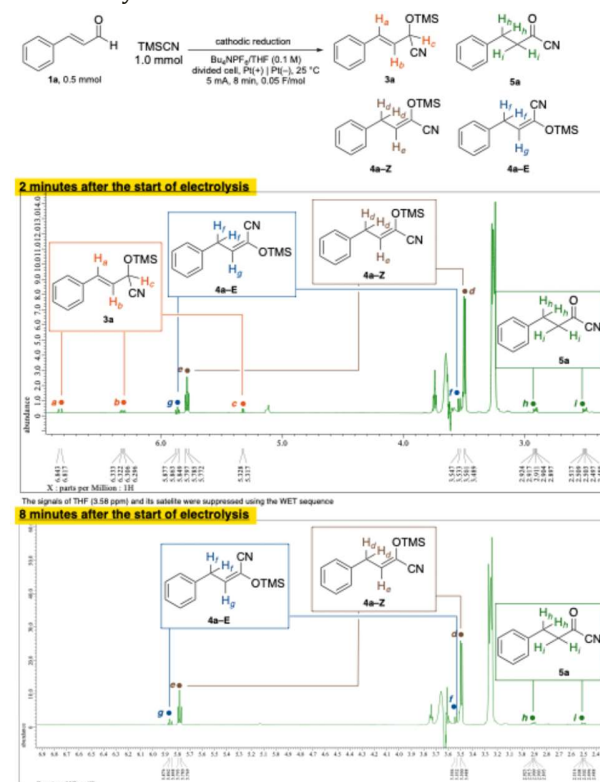
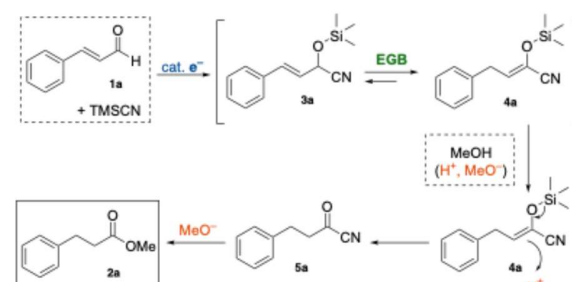


Figure 1. Direct NMR analysis of the reaction solution (600 MHz, Tetrahydrofuran-*d*₈)

Scheme 5. Proposed Mechanism



In conclusion, we have developed an electrochemical transformation of α,β -unsaturated aldehydes to carboxylic acid derivatives. This reaction sequence proceeds by a series of cyanosilylation, isomerization, and nucleophilic addition. The results of several control experiments indicate that the driving force of the reaction sequence could be the electro-generated base.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental data, spectroscopic data for all compounds, and the copies of ^1H and ^{13}C NMR spectra. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors, and all authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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