Electrochemistry

An Electrolytic System That Uses Solid-Supported Bases for In Situ Generation of a Supporting Electrolyte from Acetic Acid Solvent**

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Electroorganic synthesis is one of the most useful methods in organic synthesis and is even applied in large-scale industrial processes.[1] It has recently attracted much interest as an environmentally friendly method because electrodes are inherently environmentally friendlier reagents than conventional oxidizing and reducing reagents. However, large

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[**] This work was supported by the Nissan Motor Co., the Mizuho Foundation for the Promotion of Sciences, the foundation "Hattori–Hokokai", and the Venture Business Laboratory of the Tokyo Institute of Technology.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200500977

amounts of supporting electrolytes are necessary to provide sufficient electrical conductivity to the solvents for electrolyses. Therefore, after the electrolyses, separation of the supporting electrolytes is required, and these separated supporting electrolytes generally become industrial waste because they are mostly unrecyclable, except for some industrialized cases.[2] Furthermore, the inefficient separation of supporting electrolytes from solvents requires a huge consumption of energy and produces large amounts of additional industrial waste.

To solve such separation and industrial-waste problems, a capillary-gap cell,[3] distillation of supporting electrolytes,[2] solid polymer electrolytes,[4] electrochemical microreactors,[5] and a thin-layer flow cell[6] have been developed. To the best of our knowledge, an ideal electroorganic synthetic system from the viewpoint of green sustainable chemistry should be one that does not require the addition of any supporting electrolytes. Although solid polymer electrolytes, electrochemical microreactors, and the thin-layer flow cell provide such an ideal electroorganic synthetic system, they require special equipment.

It is well known that electron transfer between one solid and another is very difficult.[7] Therefore, it can be expected that solid-supported bases should act as bases in bulk solutions and at the same time be electrochemically inactive reagents at an electrode surface. In the presence of solid-supported bases such as amines, protic organic solvents such as acetic acid should dissociate into anions and protons to some extent [Eqs. (1) and (2)]. This system would be suitable for electroorganic synthesis because the protons derived from the protic organic solvent would play the role of the main carrier of an electronic charge via ammonium ions [Eq. (2)].[8] In this system, protic organic solvents would therefore serve both as a solvent and a supporting electrolyte generated in situ. We report herein a novel electrolytic system using solid-supported bases for the generation of a supporting electrolyte in situ from acetic acid as the solvent.

(1)

(2)

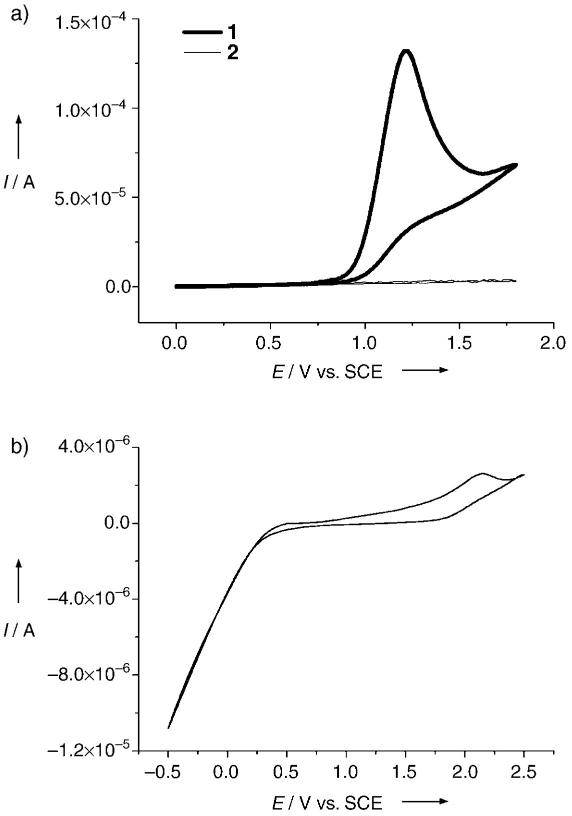


Figure 1. Cyclic voltammograms of a) *N*-methylmorpholine (**1**, 0.1 M) and polystyrene-supported morpholine (**2**, 0.1 M) in 0.1 M $n\mathrm{Bu_4NBF_4}$/MeCN, and b) AcOH/MeCN (50/50 v/v) in the presence of **2** (0.1 M) recorded at a Pt disk anode ($\phi = 0.8$ mm). The scan rate was 100 mV s^{-1}.

The cyclic voltammograms of *N*-methylmorpholine (**1**) and polystyrene-supported morpholine (**2**) were first measured in $n\mathrm{Bu_4NBF_4}$/anhydrous acetonitrile. As shown in Figure 1a, **1** is easily oxidized at around 1.2 V vs. SCE, while **2** is not oxidized at all, even when stirring. This means that solid-supported bases are not oxidized at the electrode surface. Next, the cyclic voltammogram of **2**/AcOH (0.1M based on the concentration of morpholine) was measured; however, and rather unexpectedly, neither an oxidation current nor a reduction current was observed. Acetonitrile was then added as a co-solvent and the cyclic voltammogram of 0.1M **2**/AcOH/MeCN was measured. As shown in Figure 1b, both an oxidation wave for AcO$^-$ at about 2.1 V vs. SCE and a reduction current for H$^+$ were observed.[9] Therefore, it is clear that solid-supported bases cause acetic acid to dissociate into acetate anions and protons, and the resulting protons seem to act as the main carrier of the electronic charge.

We then investigated anodic α-acetoxylation using solid-supported bases with phenyl 2,2,2-trifluoroethylsulfide (**3**)[10] as the model compound as anodic acetoxylation is one of the most useful reactions in electroorganic synthesis.[11] The overall experimental procedure is illustrated in Figure 2.

The results with various solid-supported bases are shown in Table 1; polystyrene-supported morpholine gave the α-acetoxylated product **4** in low yield (entry 1), while similar

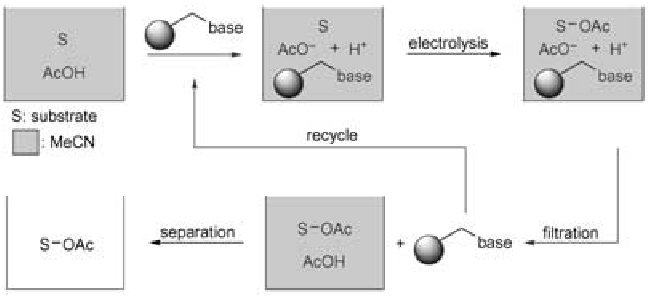
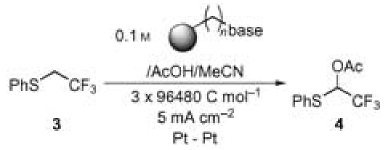
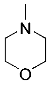
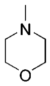
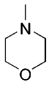
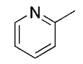
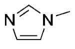
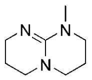


Figure 2. Schematic presentation of the experimental procedure.

Table 1: Anodic acetoxylation of **3** with various solid-supported bases.



Entry	Solid	*n*	Base	Yield[a] [%]
1	PS[b]	1	 pK_a = 8.33	39
2	PS[c]	2		81 (77)[d]
3	SiO$_2$[e]	3		72 (68)
4	SiO$_2$	3	 pK_a = 5.22	24
5	SiO$_2$	3	 pK_a = 6.95	56 (54)
6	SiO$_2$	3	 **5** pK_a = 24.3	25

[a] ^{19}F NMR spectroscopically determined yield based on the CF$_3$ group and using monofluorobenzene as an internal standard. [b] Polystyrene. [c] Porous polystyrene. [d] Yield of isolated product in parentheses. [e] Silica gel.

reactions with porous polystyrene-supported and silica gel supported morpholine proceeded efficiently to provide **4** in good to high yields (entries 2 and 3). These results indicate that the solvent compatibility of the solids is highly significant. The acetoxylated product **4** was obtained in only 24 % yield with silica gel supported pyridine, whose basicity is lower than that of morpholine (Table 1, entry 4), which means it does not dissociate acetic acid into acetate anions and protons efficiently. On the other hand, the acetoxylated product **4** was formed in 56 % yield with silica gel supported imidazole (Table 1, entry 5). Unexpectedly, anodic acetoxylation of **3** resulted in a low yield (25 %; Table 1, entry 6) when silica gel supported **5** was used, even though its basicity is much higher than that of morpholine. This can be explained as follows. Silica gel supported **5** can dissociate acetic acid into acetate anions and protons efficiently; however, **5** is protonated by the resulting protons because it is strongly basic. Therefore, the equilibrium of Equation (2) shifts to the left, and the resulting proton mobility is much lower than those of the other bases.[12]

Anodic acetoxylation of **3** was successfully carried out 10 times after recycling of the silica gel supported morpholine. In this recycling process, silica gel supported morpholine is easily separated and recovered by simple filtration (Figure 2). As shown in Figure 3, the yield of **4** was always more than 65 % and did not decrease at all upon reuse of the silica gel supported morpholine. This clearly shows that solid-supported bases are not subject to oxidative decomposition at the electrode surface and therefore recyclable many times.

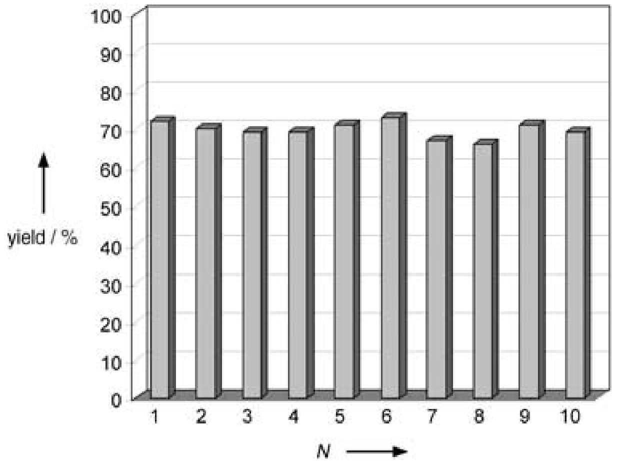
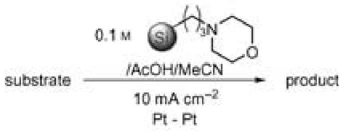
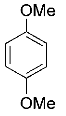
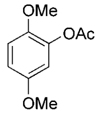
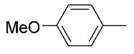
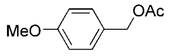
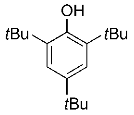
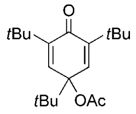


Figure 3. Yield of acetoxylated product **4** depending on the number *N* of reuses of the silica gel supported morpholine.

The generality of the new electrolytic system is shown in Table 2. Anodic acetoxylation of **6** was carried out to provide the corresponding acetoxylated product **7** in excellent yield. Anodic benzylic acetoxylation of **8** also proceeded to provide the acetoxylated product **9** in good yield. Furthermore, anodic acetoxylation of **10**, a phenol derivative, took place to provide the acetoxylated product **11** in excellent yield.

Table 2: Anodic acetoxylation of various compounds with silica gel supported morpholine.



Entry	Substrate	Electricity [×96480 C mol^{-1}]	Product	Yield[a] [%]
1	 **6**	6	 **7**	91
2	 **8**	6	 **9**	72[b]
3	 **10**	5	 **11**	95

[a] Yield of isolated product. [b] The benzylic diacetoxylated product was also formed.

In conclusion, we have developed a novel electrolytic system for anodic acetoxylation that uses solid-supported bases. This system has many practical advantages and characteristics. For instance, it does not require addition of supporting electrolytes as the supporting electrolyte is generated in situ from acetic acid as the solvent. Furthermore, it allows a simple separation of the acetoxylated products and solid-supported bases by filtration, and the solid-supported bases are electrochemically stable and recyclable. The limitations of this new methodology and its further application for electroorganic synthesis are now under investigation. In addition, we plan to apply this system to a capillary-gap cell to reduce the high internal resistance compared with conventional methods.

Received: March 17, 2005
Revised: April 19, 2005

Keywords: acetoxylation · electrochemistry · electroorganic synthesis · green chemistry · solid-supported base

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