Communication

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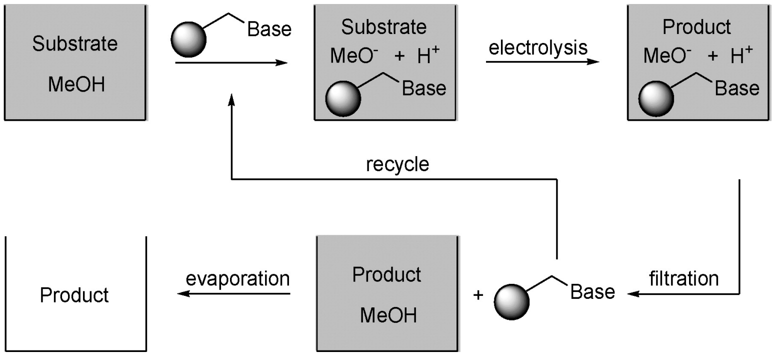

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Development of an Electrolytic System Using Solid-Supported Bases for in Situ Generation of a Supporting Electrolyte from Methanol as a Solvent

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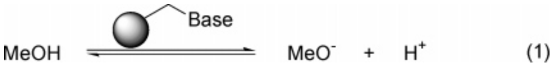
Electroorganic synthesis is one of the most useful methods in organic synthesis.[1] For example, the electrohydrodimerization of acrylonitrile to adiponitrile, an intermediate to nylon 66, originally developed by Monsanto Co. in the early 1960s, is now operating at several sites worldwide. In addition, electroorganic synthesis is an environmentally friendly process because electrons are inherently environmentally friendly reagents compared with conventional oxidizing and reducing reagents. Therefore, electroorganic synthesis has potential as a "green sustainable" process. However, large amounts of supporting electrolytes are required in order to provide sufficient electrical conductivity to solvents for electrolyses. Therefore, it is necessary to separate the supporting electrolytes from the solvents after the electrolysis, and the separated supporting electrolytes generally become industrial waste because they are mostly unrecyclable. Furthermore, the inefficient separation of supporting electrolytes from solvents results in a huge consumption of energy and large amounts of additional industrial waste. To solve such separation and industrial waste problems, it is most important to develop a novel electrolytic system not requiring the addition of any supporting electrolytes.

A capillary gap cell has been developed to minimize addition of supporting electrolytes.[2] On the other hand, solid polymer electrolytes[3] and thermomorphic biphasic electroorganic synthesis[4] have been developed to eliminate steps for the separation of supporting electrolytes. Furthermore, very recently, a thin-layer flow cell has also been developed to conduct electroorganic synthesis without intentionally added supporting electrolytes.[5]

An ideal electroorganic synthetic system from the viewpoint of green sustainable chemistry should be an electrolytic system not requiring the addition of any supporting electrolytes as well as a totally closed electrolytic system. On the other hand, it is well known that electron transfer between solid and solid is very difficult.[6] Therefore, it can be expected that solid-supported bases play the role of bases in bulk solutions as well as electrochemically inactive reagents at an electrode surface. In the presence of solid-supported bases, protic organic solvents such as methanol would be dissociated into anions and protons to some extent (eq 1). This system would be suitable for electroorganic synthesis because the protons derived from protic organic solvents would act as the main carrier of an electronic charge. In this system, protic organic solvents would serve as both a solvent and a supporting electrolyte generated in situ. Herein, we report a novel electrolytic system using solid-supported bases for in situ generation of a supporting electrolyte from a methanol solvent.



$$\mathrm{MeOH} \xrightleftharpoons{\text{Base}} \mathrm{MeO^-} + \mathrm{H^+} \qquad (1)$$

At first, the cyclic voltammograms of *N*-methylpiperidine (**1**) and polystyrene-supported piperidine **2** were measured in 0.1 M n-Bu_4N-BF_4/anhydrous acetonitrile. As shown in Figure 1a, **1** was easily oxidized at ca. 1.3 V vs SCE, while **2** was not oxidized at all, even under stirring. This means that solid-supported bases are not oxidized at the electrode surface. Next, **2** was added into methanol (0.1 M based on the concentration of piperidine), and the cyclic voltammogram of this solution was measured. As shown in Figure 1b, the oxidation wave for MeO^- at ca. 1.0 V vs SCE and the reduction current for H^+ were observed. Therefore, it is clear that methanol is dissociated into methoxide anions and protons in the presence of solid-supported bases, and the resulting protons seem to be the main carrier of an electronic charge.

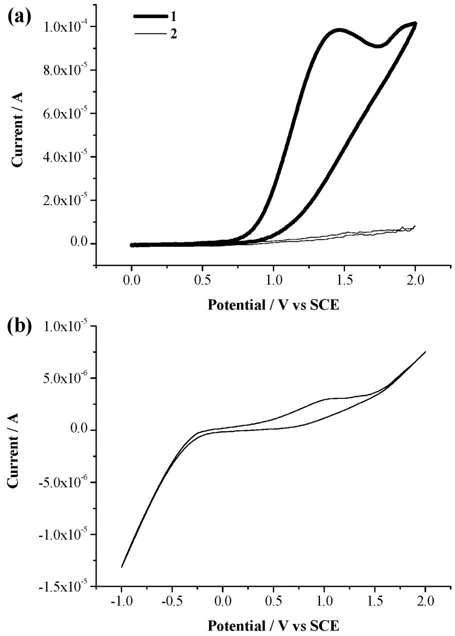


Figure 1. Cyclic voltammograms of (a) *N*-methylpiperidine (100 mM) and polystyrene-supported piperidine (100 mM) in 0.1 M n-Bu_4N-BF_4/MeCN and (b) methanol in the presence of polystyrene-supported piperidine (0.1 M), recorded at a Pt disk anode ($\phi = 0.8$ mm). The scan rate was 100 mV s^{-1}.

Next, we investigated anodic α-methoxylation using solid-supported bases. As a model reaction we chose the anodic methoxylation of phenyl 2,2,2-trifluoroethyl sulfide (**3**).[7] Anodic methoxylation processes,[8] such as 2,5-dimethoxylation of furans, anodic benzylic methoxylation of aromatic compounds, and α-methoxylation of organonitrogen compounds, are performed widely in organic synthesis and on an industrial scale. The overall experimental procedure is illustrated in Figure 2.

Anodic methoxylation of **3** was carried out using various solid-supported bases. As shown in Table 1, anodic methoxylation using polystyrene-supported piperidine took place to provide the methoxylated product **4** in low yield (entry 1), while anodic methoxylation proceeded efficiently using porous polystyrene-supported and

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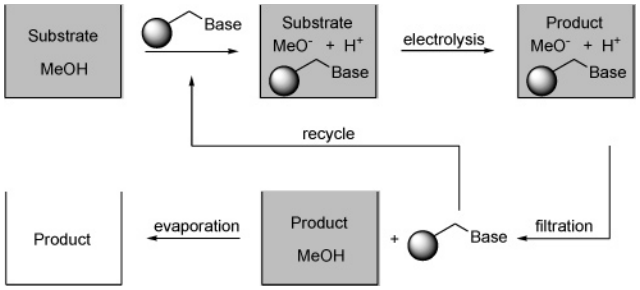
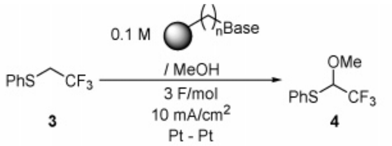
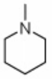
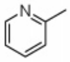
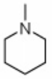
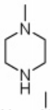
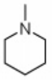
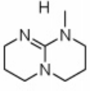


Figure 2. Experimental procedure.

Table 1. Anodic Methoxylation of **3** Using Various Solid-Supported Bases



entry	solid	n	base	yield[a] (%)	entry	solid	n	base	yield[a] (%)
1	PS[b]	1		39	4	SiO_2	3		52
2	PS[c]	2		92 (87)[e]	5	SiO_2	3		89 (84)
3	SiO_2[d]	3		76 (73)	6	SiO_2	3		70

[a] ^{19}F NMR yield based on the CF_3 group using monofluorobenzene as an internal standard. [b] Polystyrene. [c] Porous polystyrene. [d] Silica gel. [e] Isolated yield in parentheses.

silica gel-supported piperidine to provide **4** in good to excellent yields (entries 2, 3). These results indicate that the solvent compatibility of solids is highly significant. The methoxylated product **4** was obtained in 52% yield using silica gel-supported pyridine, whose basicity is much lower compared with that of piperidine (entry 4). In this case, silica gel-supported pyridine did not dissociate methanol into methoxide anions and protons efficiently since the cell voltage was higher than 50 V. On the other hand, the methoxylated product **4** was formed in high yields using strong silica gel-supported bases (entries 3, 5, and 6). Thus, it was found that relatively strong bases are suitable for the dissociation of methanol and anodic methoxylation. It is notable that the current efficiency for the anodic methoxylation of **3** was greatly increased about 3 times compared with our previous work.[7] In addition, as shown in Figure 2, the methoxylated product and solid-supported bases were easily separated by only filtration without neutralization.

Anodic methoxylation of **3** was successfully carried out 10 times by the recycling of silica gel-supported piperidine. In the recycling process, silica gel-supported piperidine was easily separated and recovered by only filtration and reused (Figure 2). As shown in Figure 3, the yield of **4** was always more than 70% and did not decrease at all upon the reuse of silica gel-supported piperidine. In addition, the appearance of silica gel-supported piperidine did not change at all before and after electrolysis. This clearly suggests that solid-supported bases are recyclable because solid-supported bases are not subject to oxidative decomposition at the electrode surface.

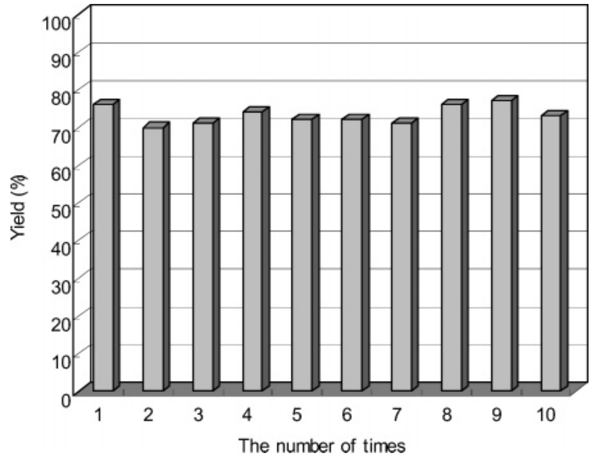


Figure 3. Yield of methoxylated product **4** in the reuse of silica gel-supported piperidine.

In conclusion, we have developed a novel electrolytic system for anodic methoxylation using solid-supported bases. This system has many practical advantages and characteristics: (a) an electrolytic system without intentionally added supporting electrolytes; (b) a supporting electrolyte generated in situ from a methanol solvent; (c) simple separation of the methoxylated product and solid-supported bases by only filtration without neutralization; (d) electrochemical stability and recyclability of solid-supported bases. Limitations of this new methodology and the further application for electroorganic synthesis are now under investigation.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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