Intramolecular acceleration effect of a tosylamide group on the electrochemical oxidation of *N*-α-silylalkyl amides

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In electrochemical oxidation, *N*-alkyl-*N*-α-silylalkyl (*N*-tosyl)amino acid amides react faster than *N*-alkyl-*N*-α-silylalkyl aliphatic amides. This phenomenon is due to the two roles of the tosylamide moiety. One is the assistance in release of the silyl cation by the tosylamide moiety to transform the cation radical, which possesses a higher oxidation potential, to the radical which possesses a lower oxidation potential. Another is the stabilization of the cation radical by the coordination of the tosylamide moiety to the positively charged silyl atom of the cation radical to shift the equilibrium of the first one-electron oxidation to the more stable side.

Introduction

Organonitrogen compounds are important as precursors in the synthesis of biologically active compounds such as alkaloids, pharmaceuticals and agrochemicals. In the chemical transformation of organonitrogen compounds to such chemicals, activation of a carbon atom alpha to nitrogen is often necessary. For this purpose, alkoxylation on an α-carbon atom of an amide or carbamate nitrogen atom by electrochemical oxidation is a versatile method.[1] We modified this method, and succeeded in stereoselective electrochemical alkoxylation on the α-carbon of an amide nitrogen atom by use of lactic acid derivatives as the acid part of the amides (Chart 1).[2]

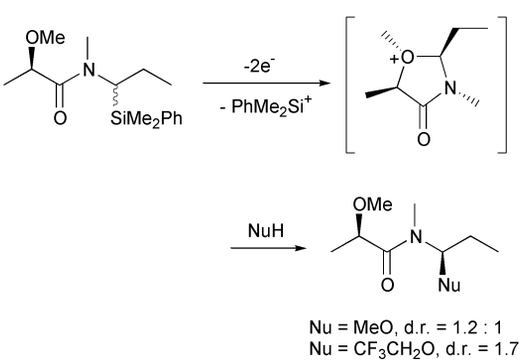

Chart 1

In this reaction, the stereoselectivity is affected by the relative nucleophilic strength of the methoxy group of the lactic acid as the internal nucleophile compared with the external nucleophilic alcohol. For alkoxylation to proceed stereoselectively, the internal nucleophilic methoxy group should attack the electrochemically generated iminium cation to yield the cyclic oxonium ion intermediate in preference to any attack by the external nucleophile. Therefore, in order to improve the stereoselectivity, a stronger internal nucleophile is necessary. On the basis that a nitrogen atom is more nucleophilic than an oxygen atom, the nitrogen-homologue of lactic acid derivatives, *i.e.*, amino acid derivatives, was examined as the acid part of the amides (Chart 2).[3]

Yoshida *et al.* reported that in electrochemical oxidation of silyl compounds, an intramolecular pyridinyl group coordinates

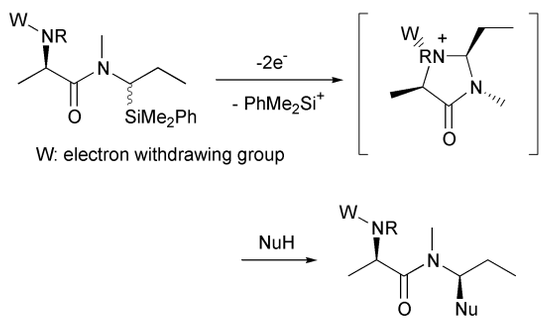

Chart 2

to the positively charged silyl atom to lower its oxidation potential.[4] The amino acid amides shown in Chart 2 are also silyl compounds which possess nitrogen substituents. For these compounds, we examined whether the same coordination effect would be observed, and if an acceleration effect in the electrochemical oxidation would be observed. We will report in this paper about the acceleration effect in detail.

Results and discussion

In the generation of imines and iminium cations by electrochemical oxidation, the protection of amines with electron-withdrawing groups as amides or carbamates prior to oxidation is necessary.[5] In the use of an amino acid as a protecting group for amines, the amino group of the amino acid must also be protected. The protecting group must be resistant to electrochemical oxidation, and stable under acidic and basic conditions, because the vicinity of electrodes is usually acidic or basic. The tosylamide group should be stable under such conditions, and was proved to be more nucleophilic than carbamates by our previous study.[3] For these reasons, tosylation was adopted as protection for the amino group of amino acids.

First, in order to confirm the effectiveness of tosylation to protect the amino group of amino acids in electrochemical oxidation, a competitive electrochemical oxidation between **1** and **2** was carried out; **2** was oxidized to decomposition products selectively, whereas **1** was recovered quantitatively (Table 1, entry 1).

The electron-withdrawing character of the tosyl group is stronger than that of the acetyl group. Therefore, the oxidation

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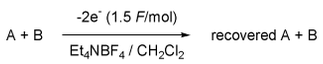
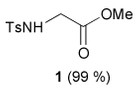
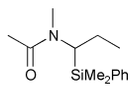
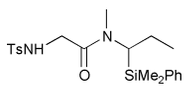
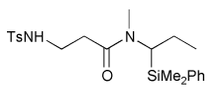
Table 1 Competitive reactions in the absence of methanol[a]



Entry	Substrates (recovered ratio)	
1	 **1** (99 %)	 **2** (70 %)
2	**2** (99%)	 **3** (70 %)
3	**2** (92%)	 **4** (75 %)
4	**3** (59%)	**4** (100%)

[a] Conditions: see experimental part.

potential of an *N*-alkyltosylamide should be higher than that of an *N*-alkylacetamide. Furthermore, the interaction between a 3d-orbital of a silyl atom and the π electrons of amide nitrogen atom in **2** lowers the oxidation potential of amides.[6] As a result of these two factors, the oxidation potential of **2** becomes lower than that of **1**, and only **2** was oxidized.

To confirm that the oxidation potential of **1** is higher than that of **2**, the cyclic voltammetry for **1** and **2** was measured (Fig. 1).

Substrate **2** showed a peak of oxidative current at 1.3 V *vs.* Ag/Ag^+, while **1** showed no oxidative current below 1.8 V *vs.* Ag/Ag^+.

From the above results, the effectiveness of tosylation to protect the amino group in the electrochemical oxidation of *N*-α-silylalkyl aliphatic amide has been proved.

Next, in order to examine the electrochemical effect of an intramolecular tosylamide moiety, a competitive electrochemical oxidation between **2** and **3** was carried out (Table 1, entry 2).

After 1.5 F mol^{-1} of electricity for **2** and **3** was passed, 30% of **3** was oxidized, and **2** was recovered quantitatively. These two substrates have the same reaction center, *N*-α-(dimethylphenyl)silylalkyl amide structure.[7] The presence or absence of an intramolecular tosylamide moiety, causes the different electrochemical behavior between **2** and **3**.

In order to confirm this hypothesis, another competitive reaction between **2** and **4** was carried out, and resulted in selective oxidation of **4** (Table 1, entry 3).

In another competitive reaction between **3** and **4**, **3** was oxidized preferentially (Table 1, entry 4).

To summarize these competitive reactions, the order in the reactivities of **2**, **3** and **4** under electrochemical oxidation is revealed as shown in Fig. 2.

In the absence of external nucleophiles, electrochemical oxidation of **2**, **3** and **4** yielded tarry compounds. In order to obtain products, a competitive reaction between **2** and **3** in the presence of methanol as an external nucleophile was carried out (Chart 3). In addition to a small amount of tarry compounds, *N*-methylacetamide **5**[8] from **2**, and a methoxylated compound **6** from **3** were obtained, whereas the selectivity observed in the absence of external nucleophiles disappeared.

Some selective electrochemical oxidations proceed as the result of the selective adsorption of substrates onto the electrode surface.[9] In our cases, the disappearance of the selectivity in the presence of methanol means that the selective adsorption of substrates onto the electrode surface is not the main factor for the selectivity.

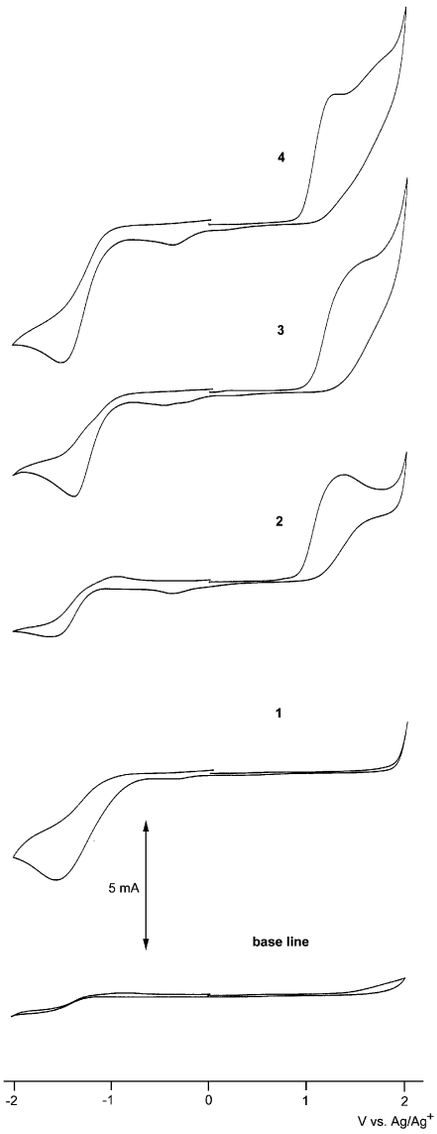


Fig. 1 Cyclic voltammetry of **1**, **2**, **3** and **4** in the absence of methanol. Conditions; [sub] = 0.01 M, $[Et_4NBF_4]$ = 0.05 M in acetonitrile, scan rate = 50 mV s^{-1}, working electrode (W.E.); 2 × 1 cm^2 Pt plate, counter electrode (C.E.); 2 × 1 cm^2 Pt plate, reference electrode (R.E.); Ag/$AgNO_3$/MeCN (BAS RE-5).

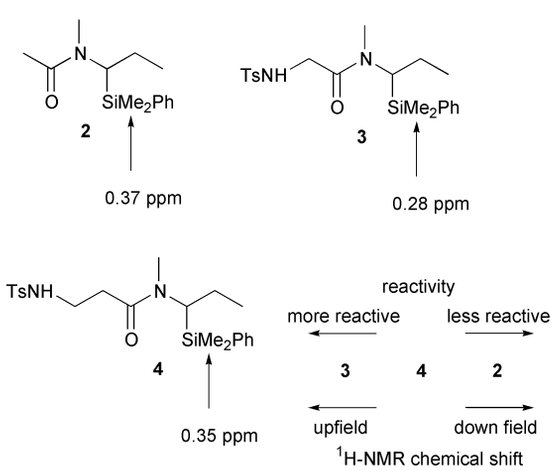


Fig. 2 The order of reactivities and ^{1}H-NMR chemical shift of the methyl on the silyl atom.

Substrates **3** and **4**, which possess a tosylamide moiety, were electrochemically oxidized predominantly over **2**, which does not possess a tosylamide moiety. This fact indicates that the

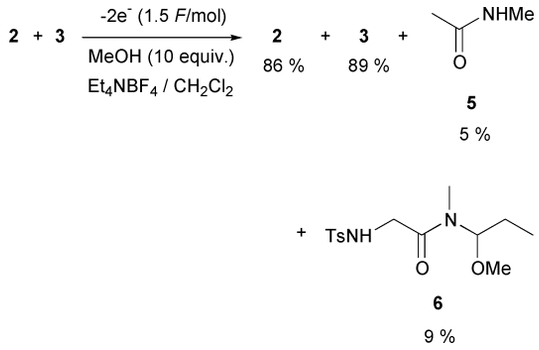


Chart 3

intramolecular tosylamide moiety makes the reaction center more sensitive to electrochemical oxidation.

Substrate **3** was oxidized in preference to **4**, which indicates that the reactivity is affected by the spatial distance between the tosylamide moiety and the reaction center. In such a case, the tosylamide moiety may act as an electron carrier from anode to the reaction center. However, oxidation at the tosylamide moiety does not occur prior to the oxidation of the reaction center, because the cyclic voltammetry measurement of **1** and **2** suggests that the oxidation potential of the tosylamide moiety should be higher than that of the reaction center (Fig. 1).

It is reported that an intramolecular interaction toward the reaction center at which electron transfer occurs, affects the redox potential of the molecule.[10] If such an interaction exists between the tosylamide moiety and the reaction center, the tosylamide moiety should interact with the silyl atom, the most positive atom in the reaction center. As a result, the environment around the silyl substituent of **3** and **4** should alter compared with **2**. To evaluate this interaction, ^{1}H-NMR chemical shifts of the methyl group on the silyl atom in **2**, **3** and **4** were measured (Fig. 2).[11]

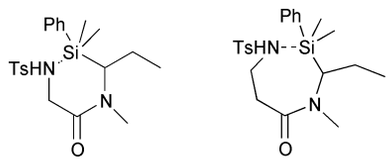
Although the extent of the upfield shift was small, the upfield shift effect was in the same order as the reactivity. The extent of upfield shift of the most reactive **3** compared with **2** is one order larger than that of **4**. This result shows that the tosylamide moiety interacts weakly with the silyl atom in the same molecule, and it is not clear whether such a weak interaction could alter the reactivity.

Yoshida *et al.* reported the effect of "dynamic coordination": if the electrostatic interaction is weak before the electron transfer process, the larger the charge increases in the process, the stronger the interaction becomes.[12] In his case, the stabilization of the electron-transfer product by the dynamic coordination makes the oxidation potential of the substrate lower. Similarly, if the dynamic coordination occurs in the cases of **3** and **4**, their oxidation potentials should be appreciably different from that of **2**.

To examine this, cyclic voltammetry of **3** and **4** was measured (Fig. 1). Substrates **3** and **4** showed a peak of oxidative current at 1.3 V *vs.* Ag/Ag$^+$, therefore, there is no difference in oxidation potential among **2**, **3** and **4**. This means that in the case of **3** and **4**, there is no "dynamic coordination effect" on the oxidation potentials.

Although a clear deviation of the oxidation potentials was not observed, the electrostatic interaction between the tosylamide moiety and the silyl atom in the reaction center would become stronger after the first single electron oxidation. Therefore, the first intermediate, a cation radical, would be stabilized in the oxidation of **3** and **4**, while the cation radical of **2** would not be stabilized. Because of the similar oxidation potentials of **2**, **3** and **4** as shown in Fig. 1, an intersubstrate electron transfer "electron scrambling" between the starting materials and their cation radicals may occur, so that the substrate which yields more stable cation radical is oxidized selectively in the competitive oxidation (Scheme 1).

This explanation is supported by the experiments in the presence of methanol, in which the selectivity disappeared. Because methanol is more silanophilic than the tosylamide moiety, the cation radicals of **2** and **3** are equally stabilized. The fact that substrate **3** was oxidized predominantly over **4** means that the cation radical of **3** in a six-membered cyclic structure is more stable than that of **4** in a seven-membered cyclic structure (Fig. 3).



3 **4**

Fig. 3 Intramolecular interaction between the tosylamide moiety and the silyl atom.

Todd *et al.* reported that in photochemical oxidation of benzyltrialkylsilane, a nucleophile assists carbon–silane bond cleavage *via* an S_N2-like mechanism to suppress the back-electron transfer process and accelerate the photochemical oxidation process.[13]

Certain *N*-silylamides are used as silylating reagents.[14] Analogously, the tosylamide moiety must be a good silanophile and *N*-silyltosylamide should be stable. It is therefore also possible that the intramolecular tosylamide moiety attacks the positively charged silyl atom in the cation radical *via* an S_N2-like mechanism to assist the carbon–silane bond cleavage.

The cation radicals of **3** and **4**, which possess the tosylamide moiety, are quickly converted to the iminium radical to suppress the back-electron transfer; in the case of **2** the back-electron transfer is not suppressed. Consequently, *via* an electron scrambling among the substrates in the first oxidation, the substrate in which the back-electron transfer is effectively suppressed is converted to the iminium radical preferentially (Scheme 1).

Once the iminium radical, which possesses a more negative oxidation potential than the starting material, is selectively produced, the subsequent oxidation to an iminium cation proceeds.

This is also the reason why the selectivity disappeared in the presence of methanol. In this case, the carbon–silane bond cleavage is assisted by the more silanophilic methanol, not by the tosylamide moiety.

In the absence of an external nucleophile, electrochemical oxidation of **2**, **3** and **4** yielded tarry products. In the presence of trifluoroethanol possessing lower nucleophilicity than methanol, **3** yielded **7** where the tosylamide moiety attacked the electrochemically generated iminium ion as an internal nucleophile (Chart 4).

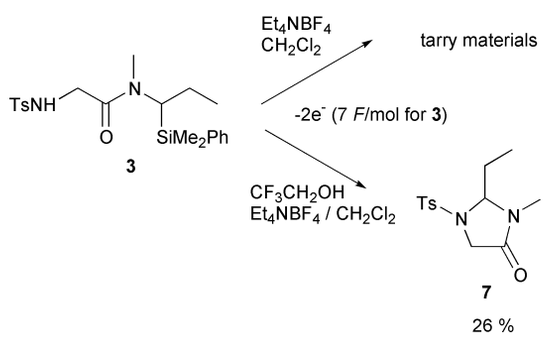
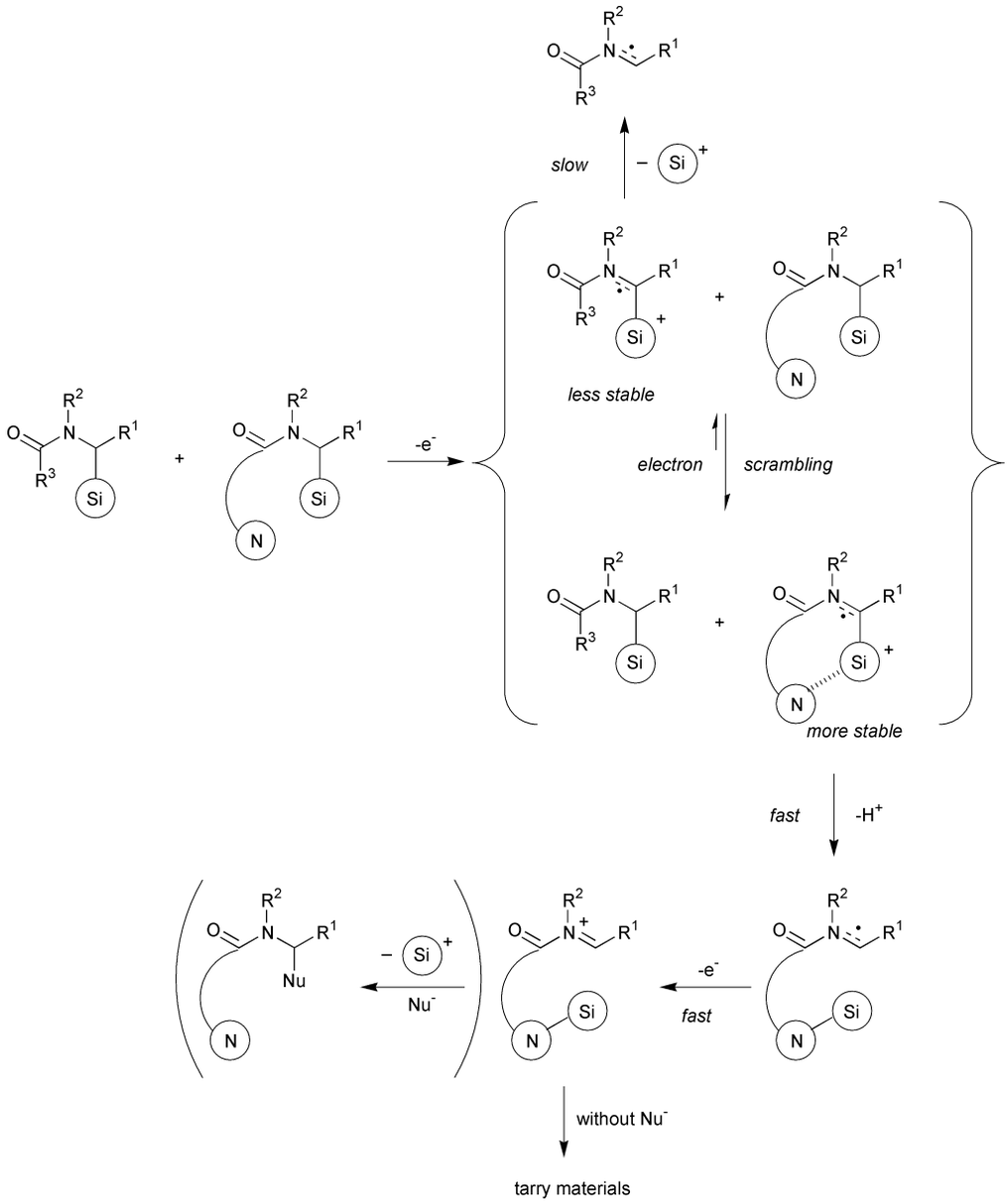


Chart 4

Thus, the tosylamide moiety exhibits nucleophilicity in the presence of trifluoroethanol in the electrochemical oxidation of **3** to give **7**.[15] These results suggest that in the cation radical



Scheme 1 Mechanism for the substrate selectivity in the competitive electrochemical oxidation in the absence of external silanopholes.

intermediate, the tosylamide moiety attacks the intramolecular positively charged silyl atom to assist the carbon–silyl bond cleavage resulting in an iminium radical, and the tosylamide moiety traps the silyl cation released in the reaction process, so that the nucleophilicity of the tosylamide moiety is decreased (Scheme 1). In the presence of trifluoroethanol, which is more silanophilic but less nucleophilic than the tosylamide moiety, the silyl cation trapped by the tosylamide moiety is removed by trifluoroethanol, and the tosylamide moiety recovers its nucleophilicity to yield **7**.

Conclusion

A substrate-selective electrochemical oxidation proceeds in the competitive reaction between an *N*-alkyl-*N*-α-(dimethylphenyl)-silylalkyl aliphatic amide and its analogous compounds owing to thermodynamic control and/or kinetic control. The thermodynamic control occurs in the first oxidation, the cation radical is stabilized more effectively by the intramolecular electrostatic interaction between the tosylamide moiety and the positively charged silyl atom, produced predominantly *via* an electron-scrambling. For the kinetic control, the cation radical in which the intramolecular assistance by the tosylamide moiety accelerates the release of the silyl cation is converted to the iminium radical preferentially. These two factors have been proven, in this study, to govern the substrate selectivity in the competitive electrochemical oxidation.

The effect of the tosylamide moiety disappeared in the presence of external nucleophiles (silanophiles). For the purpose of synthetic applications, the selectivity must appear in the presence of external nucleophiles. We anticipate this problem will be solved by the use of a multiphase method: the electrochemical phase is separated from the chemical phase where an external nucleophile reacts with an electrochemically generated reactive intermediate.

This selective electrochemical oxidation will be applicable for diastereomer separation of *N*-alkyl-*N*-α-(dimethylphenyl)silylalkyl amino acid amides. In diastereomers, the magnitude of the intramolecular interaction between the tosylamide moiety and the positively charged silyl atom is different for each diastereomers.

Experimental

Tetrahydrofuran (THF), dichloromethane (DCM), dimethylformamide (DMF) and triethylamine (TEA) were purified by the usual methods[16] and other commercially available chemicals were used without further purification. ^{1}H NMR and ^{13}C

NMR spectra were measured in $CDCl_3$ solutions using $CHCl_3$ (δ_H 7.26) and $CDCl_3$ (δ_C 77.0) as the internal standards. Chemical shifts (δ) are given in ppm and the coupling constants (J) are given in Hz. IR spectra were recorded on a grating IR spectrometer. High resolution mass spectra were measured by EI or CI or FAB methods. Cyclic voltammetry was measured on a potentiostat equipped with a function generator. An Ag/$AgNO_3$/MeCN electrode (BAS RE-5) was used as a reference electrode, and platinum plates (2 × 1 cm^2) were used as a working and a counter electrode.

Materials

N-(4-Methylphenyl)sulfonylglycine methyl ester 1

Compound **1** was obtained from glycine methyl ester by a general procedure.[17]

N-1-(Dimethylphenylsilyl)propyl-*N*-methylacetamide 2

To a solution of *N*-methyl-1-(dimethylphenylsilyl)propylamine[2] (1.01 g, 4.86 mmol) and dry TEA (1.10 cm^3, 7.89 mmol) in dry DCM (20 cm^3), a solution of acetyl chloride (0.37 cm^3, 5.26 mmol) in dry DCM (2 cm^3) was added at 0 °C under a N_2 atmosphere. The solution was refluxed for 1 h. Then sat. aq. $NaHSO_4$ solution (30 cm^3) was added to the solution. The organic layer was separated, and the aqueous layer was extracted with DCM (3 × 20 cm^3). The organic layer and the organic extracts were combined, dried over $MgSO_4$, and evaporated to give a residue, which was subjected to flash column chromatography (eluent 30 to 50% ethyl acetate–hexane) to afford the title compound (0.99 g, 81%): δ_H (a major isomer) 7.55 (2 H, m), 7.38 (3 H, m), 4.07 (1 H, dd, *J* 11.3 and 4.2), 2.78 (3 H, s), 2.06 (3 H, s), 1.6 (2 H, m, dqd *J* 11.3, 7.3 and 4.2), 0.86 (3 H, t, *J* 7.3), 0.38 (3 H, s), 0.35 (3 H, s); δ_C (a major isomer) 170.6, 137.5, 133.9, 129.1, 127.7, 49.0, 34.4, 21.6, 20.7, 12.3, −3.8, −3.9; ν_{max}/cm^{-1} (liq. film) 2960, 1640, 1250, 1140, 840; *m*/*z* (EI) (Found: M^+. 249.1512. $C_{14}H_{23}NOSi$ requires *M*, 249.1549).

N-[1-(Dimethylphenylsilyl)propyl]-*N*-methyl-*N*'-(4-methylphenyl)sulfonylglycinamide 3

To a solution of chloroacetyl chloride (0.57 cm^3, 7.16 mmol) in dry DCM (11.4 cm^3), a solution of *N*-methyl-1-(dimethylphenyl)silylpropylamine (1.38 g, 6.65 mmol) and dry TEA (1.39 cm^3, 9.97 mmol) in dry DCM (11.4 cm^3) was added at 0 °C under N_2 atmosphere. After stirring at ambient temperature overnight, water (30 cm^3) was added to the solution. The organic layer was separated, and the aqueous layer was extracted with DCM (2 × 30 cm^3). The organic layer and the organic extracts were combined, dried over $MgSO_4$, and evaporated to give a residue, which was subjected to flash column chromatography (eluent 20 to 40% ethyl acetate–hexane) to afford *N*-[1-(dimethylphenylsilyl)propyl]-*N*-methylchloroacetamide (1.14 g, 60%); δ_H (a major isomer) 7.50 (2 H, m), 7.36 (3 H, m), 3.99 (2 H, s), 3.98 (1 H, t, *J* 6.6), 2.85 (3 H, s), 1.64 (2 H, m, containing td, *J* 7.2 and 6.6), 0.85 (3 H, t, *J* 7.2), 0.38 (3 H, s), 0.34 (3 H, s); δ_C (a major isomer) 166.4, 137.1, 133.9, 129.3, 127.8, 49.9, 41.4, 33.9, 20.6, 12.2, −3.8, −4.0; ν_{max}/cm^{-1} (liq. film) 2960, 1650, 1400, 1255, 1140, 700; *m*/*z* (EI) (Found: M^+. 283.1150. $C_{14}H_{22}NOClSi$ requires *M*, 283.1159).

To a suspended solution of sodium hydride (60% in mineral oil) (0.25 g, 6.27 mmol) in dry DMF (2.5 cm^3), a solution of tosylamide (0.83 g, 4.82 mmol) in dry DMF (6.3 cm^3) was added at ambient temperature under N_2 atmosphere. The solution was stirred at 60 °C for 2 h, and cooled to ambient temperature. To the solution, a solution of *N*-[1-(dimethylphenylsilyl)propyl]-*N*-methylchloroacetamide (1.14 g, 4.01 mmol) in dry DMF (2.6 cm^3) was added. The solution was stirred at 60 °C for 2 h. Water (30 cm^3) was added to the solution. The solution was extracted with diethyl ether (3 × 30 cm^3). The organic extracts were combined, dried over $MgSO_4$, and evaporated to give a residue, which was subjected to flash column chromatography (eluent 20 to 40% ethyl acetate–hexane) to afford **3** (1.02 g, 61%); δ_H (a major isomer) 7.76 (2 H, d, *J* 8.3), 7.44 (2 H, m), 7.32 (2 H, d, *J* 8.3), 7.34 (3 H, m), 5.70 (1 H, br s), 3.94 (1 H, t, *J* 7.8), 3.53 (2 H, d, *J* 16.1), 2.57 (3 H, s), 2.43 (1 H, s), 1.58 (2 H, dt, *J* 7.8 and 7.2), 0.70 (3 H, t, *J* 7.2), 0.29 (3 H, s), 0.26 (3 H, s); δ_C (a major isomer) 166.3, 143.4, 133.9, 133.8, 133.6, 129.6, 129.4, 127.8, 127.2, 50.9, 43.7, 43.6, 31.9, 20.4, 12.1, −4.0; ν_{max}/cm^{-1} (KBr) 3230, 2960, 1640, 1390, 1170, 820, 710, 560; *m*/*z* (CI) (Found: M^+. 419.1822. $C_{21}H_{30}N_2O_3SSi + H^+$ requires *M*, 419.1824).

N-1-(Dimethylphenylsilyl)propyl-*N*-methyl-*N*'-(4-methylphenyl)-sulfonyl-β-alaninamide 4

β-Alanine was converted to *N*-(4-methylphenyl)sulfonyl-β-alanine by a general procedure.[17] A solution of DCC (1.01 g, 4.92 mmol) in dry DCM (4.7 cm^3) was added to a suspended solution of *N*-(4-methylphenyl)sulfonyl-β-alanine (1.17 g, 4.83 mmol) in dry DCM (60 cm^3) at 0 °C under N_2 atmosphere. After stirring for 15 min, a solution of *N*-methyl-1-(dimethylphenylsilyl)propylamine (1.01 g, 4.85 mmol) in dry DCM (4.7 cm^3) was added to the solution. After stirring at ambient temperature overnight, the resulting white solid was filtered off, and washed with DCM (30 cm^3). The filtrate and the washings were collected, and washed with water (50 cm^3). The organic portion was dried over $MgSO_4$, and evaporated to give a residue, which was subjected to flash column chromatography (eluent 20 to 80% ethyl acetate–hexane) to afford the title compound (1.99 g, 95%); δ_H (a major isomer) 7.76 (2 H, d, *J* 8.1), 7.49 (2 H, m), 7.37 (3 H, m), 7.32 (2 H, d, *J* 8.1), 5.70 (1 H, br s), 4.06 (1 H, t, *J* 9.0), 3.13 (2 H, t, *J* 5.5), 2.68 (3 H, s), 2.44 (3 H, s), 2.38 (2 H, t, *J* 5.5), 1.61 (2 H, m), 0.82 (3 H, t, *J* 7.0), 0.35 (3 H, s), 0.34 (3 H, s); δ_C (a major isomer) 170.8, 143.1, 137.1, 135.8, 133.8, 129.6, 129.3, 127.8, 127.0, 51.4, 49.0, 39.3, 33.0, 21.4, 20.6, 12.3, −3.7, −4.0; ν_{max}/cm^{-1} (liq. film) 3220, 2960, 1620, 1330, 1160, 1100, 820, 720; *m*/*z* (CI) (Found: M^+. 433.1979. $C_{22}H_{32}N_2O_3SSi + H^+$ requires *M*, 433.1981).

Competitive electrolysis of amides in the presence or absence of methanol

A solution of an amide (0.25 mmol), another amide (0.25 mmol), and tetraethylammonium tetrafluoroborate (0.043 g, 0.2 mmol) in dry DCM (4 cm^3) was placed in an undivided cell equipped with two platinum plate electrodes (2 × 1 cm^2). A constant current (20 mA) was passed in the presence of methanol (0.080 g, 2.5 mmol) or in the absence of methanol at ambient temperature under N_2 atmosphere. After 36.2 C of electricity (1.5 F mol^{-1}) was consumed, volatiles were evaporated to give a residue, which was subjected to flash column chromatography (eluent 20 to 40% ethyl acetate–hexane) to afford the unreacted amides, **5**[18] and **6**. The results were summarized in Table 1 and Chart 3.

N-(1-Methoxypropyl)-*N*-methyl-*N*'-(4-methylphenyl)sulfonylglycinamide 6

δ_H 7.75 (2 H, d, *J* 8.2), 7.28 (2 H, d, *J* 8.2), 5.72 (1 H, br s), 5.34 (1 H, t, *J* 6.8), 3.76 (2 H, d, *J* 3.5), 3.05 (3 H, s), 2.64 (3 H, s), 2.38 (3 H, s), 1.61 (2 H, m), 0.72 (3 H, t, *J* 7.5); δ_C 168.1, 143.6, 136.0, 129.7, 127.3, 86.1, 55.6, 43.8, 25.9, 25.2, 21.4, 8.9; ν_{max}/cm^{-1} (liq. film) 3250, 2980, 2950, 1660, 1400, 1360, 1340, 1170, 1100, 1070, 920, 820, 740; *m*/*z* (FAB^+, matrix; *m*-NBA) (Found: M^+. 315.1368. $C_{14}H_{22}N_2O_4S + H^+$ requires *M*, 315.1379).

Electrolysis of 3 in the presence of trifluoroethanol

A solution of **3** (0.19 g, 0.458 mmol), trifluoroethanol (0.50 g, 5.01 mmol), and tetraethylammonium tetrafluoroborate (0.043 g,

0.2 mmol) in dry DCM (4 cm^3) was placed in an undivided cell equipped with two platinum plate electrodes (2 × 1 cm^2). Constant current (20 mA) was passed at ambient temperature under N_2 atmosphere. After 7 F mol^{-1} was consumed, volatiles were evaporated to give a residue, which was subjected to flash column chromatography (eluent 10 to 80% ethyl acetate–hexane) to afford **3** (99.1 mg, 48%) and 1,4-diaza-1-methyl-2-ethyl-3-(4-methylphenylsulfonyl)cyclopentan-5-one **7** (17.6 mg, 26% to the consumed **3**): δ_H 7.70 (2 H, d, *J* 8.3), 7.34 (2 H, d, *J* 8.3), 4.97 (1 H, t, *J* 2.8), 3.86 (2 H, s), 2.67 (3 H, s), 2.44 (3 H, s), 2.04 (1 H, dtd, *J* 22.1, 7.4 and 2.8), 1.76 (1 H, dtd, *J* 22.1, 7.4 and 2.8), 0.88 (3 H, t, *J* 7.4); δ_C 167.2, 144.7, 133.3, 130.2, 127.5, 77.2, 49.6, 26.7, 26.1, 21.6, 5.9; ν_{max}/cm^{-1} (KBr) 2980, 1720, 1350, 1170, 950, 680, 600; *m*/*z* (CI) (Found: M^+. 283.1099. $C_{13}H_{18}N_2O_3S + H^+$ requires *M*, 283.1117).

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