Electro-initiated Coupling Reactions of *N*-Acyliminium Ion Pools with Arylthiomethylsilanes and Aryloxymethylsilanes

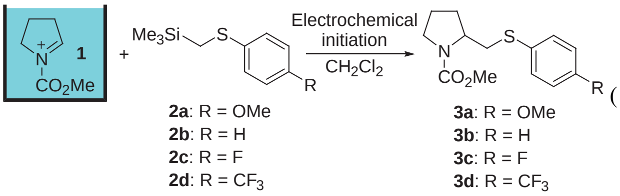
Seiji Suga, Ikuo Shimizu, Yosuke Ashikari, Yusuke Mizuno,
Tomokazu Maruyama, and Jun-ichi Yoshida*
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering,
Kyoto University, Nishikyo-ku, Kyoto 615-8510

(Received June 20, 2008; CL-080629; E-mail: yoshida@sbchem.kyoto-u.ac.jp)

Electro-initiated coupling reactions of *N*-acyliminium ion with arylthiomethylsilanes and aryloxymethylsilanes were developed. Pulse electrolyses with intervals were found to be quite effective for the initiation. A chain mechanism involving cation, radical cation, and radical intermediates has been proposed.

Electro-initiated chain reactions constitute an interesting class of reactions. Only a catalytic amount of electricity is required for completion of the reaction, because electrolysis is used for generation of a reactive species that initiates a chain process. For example, oxygenation involving a radical intermediate,[1] [2 + 2] cycloaddition,[2] and olefin metathesis[3] via radical ion intermediates, and a cation chain reaction[4] have been reported in the literature. We report herein another example of electro-initiated chain reactions, which involves cation, radical, and radical cation intermediates.

The present work stems from our earlier observations that the reactions of *N*-acyliminium ion pools with benzylsilanes proceed by a radical/radical–cation/cation crossover mechanism.[5] We examined a similar reaction of *N*-acyliminium ion pools with arylthiomethylsilanes because it is well established that the anodic oxidation of arylthiomethylsilane leads to facile cleavage of the C–Si bond (eq 1).[6]



(1)

Thus, *N*-acyliminium ion **1** was generated from the corresponding silyl-substituted carbamate by low-temperature electrolysis using Bu_4NBF_4 as a supporting electrolyte in CH_2Cl_2, and a solution of **1** was allowed to react with arylthiomethylsilane **2a** without electrochemical initiation.[7] The expected coupling product **3a** was not obtained, and most of **2a** remained unchanged. The result was surprising because the oxidation potential of **2a** seems to be low enough for the initial electron transfer (Table 1). In fact, the benzylsilanes of higher oxidation potentials reacted with **1** to give the coupling product.[5] Presumably, the C–Si bond in the radical cation is difficult to cleave. In fact, DFT calculations of a model radical cation **4a** indicate that the conformation in which the C–Si bond can interact with the p orbital of sulfur (**4av**) is less stable than the conformation in which the C–Si bond is perpendicular to the p orbital of sulfur (**4ah**), although the energy difference is small ($\Delta E =$ 0.97 kJ/mol) (Figure 1).

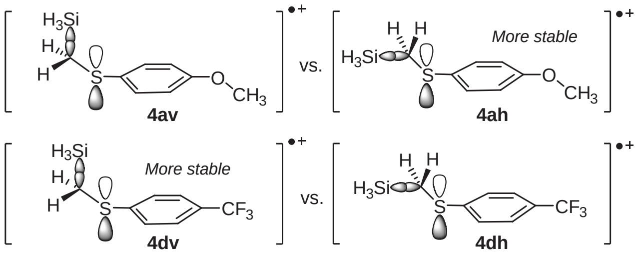


Figure 1. Structures of the model radical cations **4a** and **4d** obtained by DFT calculations (B3LYP/6-31G(d)).

Table 1. Electro-initiated reactions of *N*-acyliminium ion **1** with arylthiomethylsilanes[a]

Arylthiomethyl-silane	Oxidation potential /V	Electricity /F mol^{-1}	Product	Yield /%
2a	1.18	0	**3a**	—[b]
		0.003 × 3	**3a**	—[b]
2b	1.41	0	**3b**	14
		0.003 × 3	**3b**	46
2c	1.43	0	**3c**	27
		0.003 × 3	**3c**	69
2d	1.58	0	**3d**	45
		0.01	**3d**	72
		0.003 × 3	**3d**	90

[a]Reactions were carried out at 0 °C for 1 h. [b]The expected product **3a** was not detected.

The reaction with **2b** gave the corresponding coupling product **3b** without electrochemical initiation, although the yield was low (Table 1). The introduction of an electron-withdrawing group such as F (**2c**) and CF_3 (**2d**) improved the yield of the coupling products **3c** and **3d**.

DFT calculations indicate that **4dv** is more stable than **4dh** ($\Delta E = 3.70$ kJ/mol). The interaction with the C–Si bond stabilizes the radical cation, although such stabilization is not necessary for radical cations having a strong electron-donating group like **4a**. Such interaction weakens the C–Si bond and facilitates C–Si bond cleavage by nucleophilic attack on the silicon atom.

The present reaction seems to proceed by a chain mechanism shown in Figure 2. The initial single-electron transfer from **2** to *N*-acyliminium ion **1** gives radical cation **4** and radical **5**. The C–Si bond in **4** is cleaved to generate radical **6**.[8] This process is presumably assisted by nucleophilic attack of BF_4^-, which is the counter anion of **1**. Radical **6** thus generated adds to *N*-acyliminium ion **1** to give radical cation **7**. We have already reported that an alkyl radical adds *N*-acyliminium ion pools very rapidly.[9] Radical cation **7** undergoes a single-electron transfer reaction with **2** to give the coupling product **3** and radical cation **4**, which collapses to radical **6**.

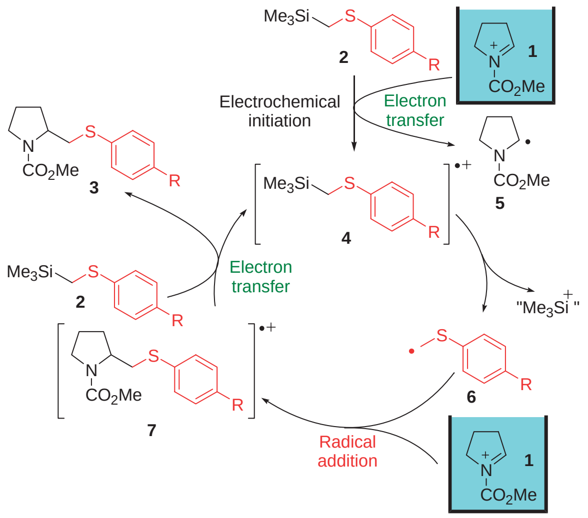
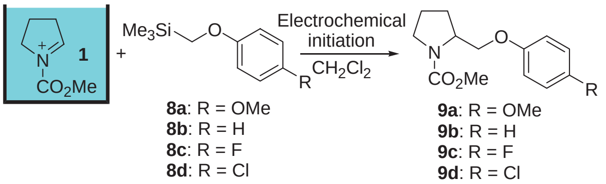


Figure 2. Proposed reaction mechanism.

Although the chain process seems to proceed effectively for compounds **2b**–**2d**, the yields of the coupling products were rather low. The initiation step seemed to be the bottleneck. To facilitate this step, we examined the electrochemical initiation.

Thus, the electrolysis of a mixture of **1** and **2d** was carried out with a catalytic amount of electricity (0.01 F/mol based on **2d**) (Table 1).[7] The yield of **3d** increased significantly (72%). Three pulse electrolyses with 20 min intervals were found to be more effective. The yield was improved to 90%. The pulse electrolyses were also effective for compounds **2b** and **2c**. However, **2a** was inactive even with the pulse electrolyses.

Aryloxymethylsilanes **8** also reacted with **1** in a similar manner to give the corresponding coupling products **9** (eq 2).



(2)

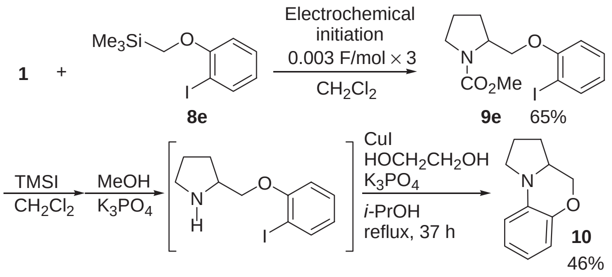
As shown in Table 2, a compound having a methoxy group on the benzene ring (**8a**) was also active although the yield was very low. Presumably the oxygen p orbital interacts with the C–Si bond more effectively to facilitate the C–Si bond cleavage.

The present method is compatible with a halogen atom such as iodine on the benzene ring. Therefore, such functionality can be utilized for further transformation. The example shown in Scheme 1 demonstrates synthetic utility of the present method.

Table 2. Electro-initiated reactions of *N*-acyliminium ion **1** with aryloxymethylsilanes[a]

Aryloxy-methylsilane	Oxidation potential /V	Electricity /F mol^{-1}	Product	Yield /%
8a	1.34	0	**9a**	trace
		0.003 × 3	**9a**	20
8b	1.64	0	**9b**	—[b]
		0.003 × 3	**9b**	10
8c	1.65	0	**9c**	14
		0.003 × 3	**9c**	80
8d	1.68	0	**9d**	52
		0.003 × 3	**9d**	quantitative

[a]Reactions were carried out at 0 °C for 1 h. [b]**9b** was not detected.



Scheme 1.

In conclusion, the present observations demonstrate that the pulse electrolyses with intervals are quite effective for initiating reactions involving cation/radical–cation/radical chain processes, and the method opens a new possibility of electron-transfer driven chain reactions.

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The authors dedicate this paper to Professor Ryoji Noyori on the occasion of his 70th birthday.

References and Notes

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