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

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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 metathesis³ via radical ion intermediates, and a cation chain reaction⁴ 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



Thus, N-acyliminium ion 1 was generated from the corresponding silvl-substituted carbamate by low-temperature electrolysis using Bu₄NBF₄ as a supporting electrolyte in CH₂Cl₂, 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).

The reaction with 2b gave the corresponding coupling



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

^aReactions were carried out at 0 °C for 1 h. ^bThe expected product **3a** was not detected.

product **3b** without electrochemical initiation, although the yield was low (Table 1). The introduction of an electron-withdrawing group such as F (**2c**) and CF₃ (**2d**) improved the yield of the coupling products **3c** and **3d**.

DFT calculations indicate that **4dv** is more stable than **4dh** $(\Delta E = 3.70 \text{ kJ/mol})$. 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 BF₄⁻, 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).



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

Table 2. Electro-initiated reactions of N-acyliminium ion 1 with aryloxymethylsilanes^a

Aryloxy- methylsilane	Oxidation potential /V	Electricity /Fmol ⁻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

^aReactions were carried out at 0 °C for 1 h. ^b9b was not detected.



Scheme 1.

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.

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.

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