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Electroreductive Synthesis of Acylsilanes from Acylimidazoles

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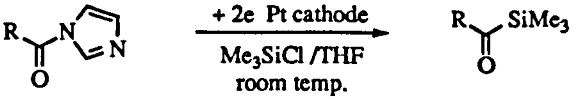
Abstract: Electroreduction of acylimidazoles in the presence of chlorotrimethylsilane gave the corresponding acylsilanes in satisfactory yields. Acylsilanes having a functional group such as an alkoxycarbonyl or chloro group also were synthesized effectively.

It is well known that acylsilanes[1] have unique reactivity and their synthetic utility is remarkably growing as evidenced by the numerous recent studies of organic synthesis utilizing acylsilanes.[2] Although many synthetic methods[1,3] have so far been developed since the first synthesis of acylsilanes by Brook,[4] more versatile methods are desired for the synthesis of acylsilanes, especially functionalized acylsilanes.[5] On the other hand, electroreductive silylation of halides[6] and activated olefins[7] have been reported by us and other groups. We report herein that the synthesis of acylsilanes is achieved effectively by electroreductive silylation of acylimidazoles (eq 1).[8,9] Since this new method can be carried out under mild conditions without use of any metal reducing agents, some functional groups such as the alkoxycarbonyl and chloro groups are not affected.

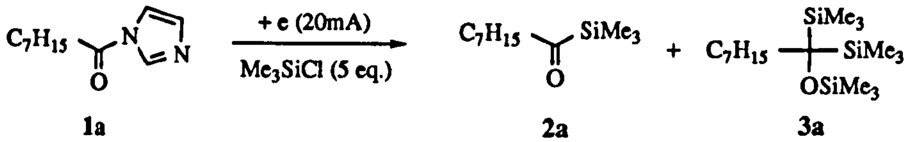


(1)

A typical procedure is as follows. Octanoylimidazole (**1a**)[10] (1 mmol), chlorotrimethylsilane (5 mmol), and a 0.5 M solution of Bu_4NClO_4 in THF (3 mL) was placed in the cathodic chamber of an H-type cell equipped with a Pt cathode and a Pt anode (2 X 1 cm^2). A 0.5 M solution of Bu_4NClO_4 in DMF (4 mL) was placed in the anodic chamber. Constant current (20 mA) was passed with stirring at room temperature. After 2.5 F/mol (241 C) of electricity was passed, the catholyte was poured into water (10 mL). Organic materials were extracted with ether and dried over $MgSO_4$. After removal of the solvent, octanoyltrimethylsilane (**2a**) (73 %) and a trace amount of 1,1-bis(trimethylsilyl)-1-octyl trimethylsilyl ether (**3a**) were isolated by column chromatography on silica gel.

Reaction conditions were surveyed with **1a** and the results are summarized in Table 1. As the solvent, THF gave better results than DMF and CH_3CN did. Although Pt, Pb, Ni, and carbon graphite could be employed as the cathode, Pt was the best cathode for the synthesis of **2a**. The reaction profile of the electroreduction of **1a** with Pt cathode in THF was drawn as Fig. 1 by GLC analysis. The yield of **2a** grew steadily, reached a peak at 2.5 F/mol, and then decreased as the yield of **3a** increased. This result suggests that **3a** was formed from **2a** by further reduction. Actually, in a separate experiment, the electroreduction of **2a** under similar conditions gave **3a**. In order to obtain the further reduced product **3a**, Pb was the cathode of choice.

Table 1. Electroreduction of Octanoylimidazole (**1a**) in the Presence of Me_3SiCl



Cathode material	Solvent of catholyte	Electricity (F/mol)	Yield (%)[a]	
			2a	**3a**
Pt	THF	2.5	73	3
Pt	DMF	4.0	56	3
Pb	THF	3.0	60	12
Pb[b]	THF	10.0	8	48
Pb	DMF	3.0	57	5
C	THF	2.5	63	9
Ni	THF	3.0	58	8

[a] Isolated yields. [b] 10 eq. of Me_3SiCl.

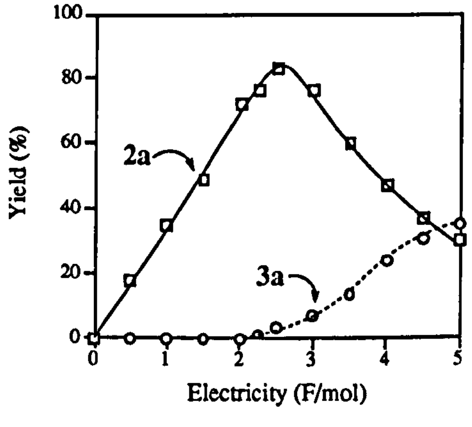
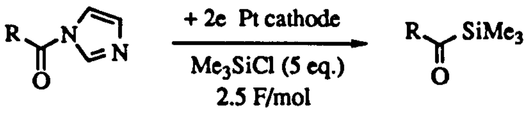


Fig. 1. Reaction Profile of Reduction of **1a** in the Presence of Me_3SiCl (5 eq.)

As shown in Table 2, other acylsilanes were also synthesized from the corresponding acylimidazoles under the same reaction conditions as above. It is noted that acylimidazoles having a functional group such as an alkoxycarbonyl or chloro group gave the corresponding acylsilanes effectively.

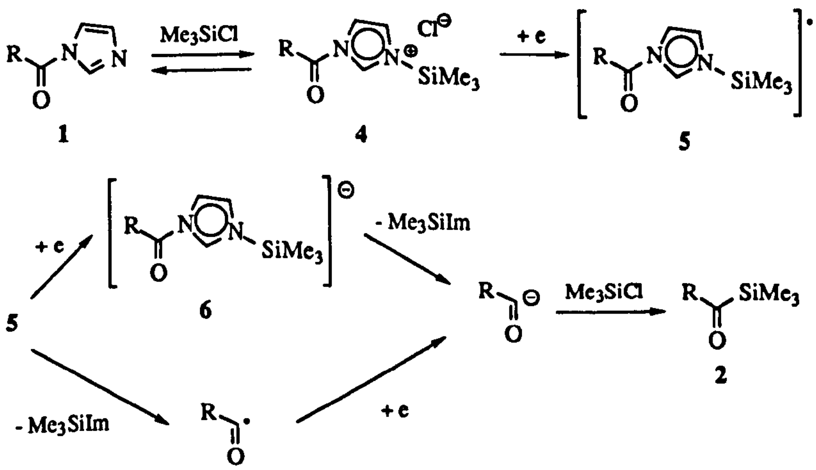
Table 2. Electroreductive Synthesis of Acylsilanes



R	Yield (%)[a]
C_7H_{15}	73
$C_{11}H_{23}$	70
$C_6H_5CH_2CH_2$	68
$C_6H_5CH_2$	54
$C_6H_5CH=CH$	35[b]
$MeO_2CCH_2CH_2$	63
$MeO_2CCH_2CH_2CH_2CH_2$	54
$ClCH_2CH_2CH_2$	67

[a] Isolated yields from acyl chlorides (ref. 10).
[b] Obtained as $C_6H_5CH_2CH_2COSiMe_3$.

The following observations seem to be helpful for the elucidation of the reaction mechanism. The addition of 1 equiv. of chlorotrimethylsilane to a solution of **1a** shifted the reduction potential of **1a** from -2.34 V to -1.38 V.[11] This result suggests that acylimidazole and chlorotrimethylsilane form salt **4**. ^1H NMR analysis of **1a** in the presence of chlorotrimethylsilane also supports the formation of **4**.[12] It can be reasonably assumed that the reaction is initiated by the reduction of **4**. Therefore, the mechanism can be speculated to be as shown in Scheme 2. Radical **5** is formed by one-electron transfer to **4** and then it is converted to an acyl anion[13] by a second one-electron transfer and elimination of trimethylsilylimidazole through anion **6** or an acyl radical. Finally, the acyl anion is silylated by chlorotrimethylsilane to give acylsilane **2**.



Scheme 2

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9. Recently, it has been reported that electroreductive silylation of aromatic acid anhydrides gave mixtures of acylsilanes and their simply reduced alcohols: Tsuruhara, T.; Ishino, Y.; Maekawa, H.; Sukata, K.; Nishiguchi, I. Preprint of 67th Annual Meeting of the Chemical Society of Japan, May 1994, p 1333.
10. Octanoylimidazole **1a** was prepared quantitatively from octanoyl chloride and imidazole (2 equiv) by stirring in THF at 0 °C for 1h. The other acylimidazoles in Table 2 were prepared in a similar manner and subjected to electroreduction without further purification.
11. Reduction potentials were determined as decomposition potentials by rotating-disk-electrode voltammetry using a platinum working electrode in 0.1 M Bu_4NClO_4/CH_3CN. SCE was used as the reference electrode. Sweep rate was 10 mV/s. Similarly, the addition of 1 equiv. of chlorotrimethylsilane to a solution of acylsilane **2a** shifted the reduction potential of **2a** from -2.48 V to -1.74 V.
12. The addition of chlorotrimethylsilane to **1a** caused significant downfield shifts of the imidazole protons of **1a**.
13. There is no evidence at present for the formation of the acyl anion. Bissilylation of the carbonyl group of 4 followed by hydrolysis is an alternative path, although such bissilylated product could not be detected in the reaction mixture by ^1H NMR and GLC analysis.

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