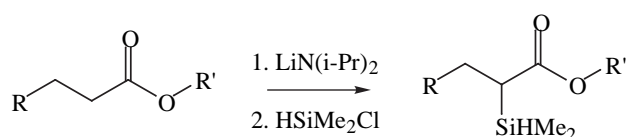


**Electrochemical Oxidation and Reduction
of *alpha*-Dimethylsilyl Esters.
A Novel Silicon *gamma*-Aryl Effect**

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- 1a**, R = C₆H₅, R' = Me
b, R = H; R' = i-Pr
c, R = Me; R' = i-Pr
d, R = *n*-Bu; R' = Me

Reaction of a series of ester enolates with dimethylchlorosilane was found to afford the corresponding *alpha*-dimethylsilyl esters, $\text{RCH}(\text{SiHMe}_2)\text{CO}_2\text{R}'$ (**1**). The substances were fully characterized by ¹H (1-D, COSY, DQ-COSY, 2-D TOCSY), ¹³C, and ²⁹Si NMR spectroscopic experiments and mass spectrometry, together with extensive molecular mechanics calculations to locate their low-lying conformation(s). Voltammetric experiments in acetone/Bu₄NPF₆ (vs. Ag/0.1M AgNO₃) established that ester **1a** is considerably easier to oxidize than the other silyl esters. This suggested that the presence of a *beta*-phenyl group facilitates oxidation of a silane. To explain the relatively low potential at which **1a** is oxidized, we suggest the operation of a hitherto unobserved “silicon *gamma*-aryl effect”, by which a *beta*-arylsilane such as **1a** is oxidized to a radical cation more readily than in the absence of the aryl group. We have carried out *ab initio* density functional computations (B3LYP/6-31G*, including solvation via the SCF-polarized solvent continuum method) on these silanes. Their computed ionization potentials and a comparison of the electron density distribution in the neutral silanes and their radical cations *and their dependence on the conformation of the silane* clearly support the incursion of the silicon *gamma*-effect with **1a** and with the closely related *beta*-phenylethyltrimethylsilane. This suggests the possibility of oxidation of ester **1a** to a species bearing a positive charge adjacent to the ester carbonyl group. Indeed, anodic oxidation of **1a** in trifluoroacetic acid at 0 °C results in the formation of methyl *alpha*-trifluoroacetoxy hydrocinnamate in 50% yield. Other examples of the silicon *gamma*-aryl effect will be discussed.

We have also studied the cathodic reduction of the silyl esters **1**. No cathodic reduction wave is observed for any of these compounds in acetonitrile/ Bu₄NPF₆ which has previously been degassed by nitrogen purge. However, when air is admitted to the medium, the height of the oxygen voltammetric reduction peak is enhanced by all of the silyl esters. This suggests that they undergo reaction with electrochemically-generated superoxide ion. This hypothesis is supported by preparative-scale electrolysis; in every case the desilylated substance $\text{RCH}_2\text{CO}_2\text{R}'$ is produced in quantitative yield.