

ELECTROREDUCTIVE HYDROCOUPLING OF ACTIVATED OLEFINS WITH KETONES OR ALDEHYDES  
IN THE PRESENCE OF TRIMETHYLCHLOROSILANE<sup>1</sup>

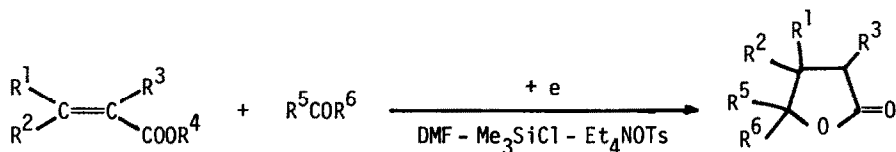
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Electroreductive crossed hydrocoupling of  $\alpha,\beta$ -unsaturated esters with aldehydes or ketones in the presence of trimethylchlorosilane afforded  $\gamma$ -lactones in good yields. Similarly  $\alpha,\beta$ -unsaturated nitriles gave  $\gamma$ -hydroxynitriles in high yields.

Cathodic crossed hydrocoupling of activated olefins such as  $\alpha,\beta$ -unsaturated esters, ketones, and nitriles with aldehydes or ketones is one of the most useful methods of synthesizing  $\gamma$ -lactones, 1,4-diketones, and their related compounds. However, only few studies<sup>2-5</sup> carried out in sulfuric acid have been reported indicating that this coupling is not interesting from the stand point of low material yields and lack of generality.

We wish to report herein a novel electroreductive crossed hydrocoupling of activated olefins with ketones or aldehydes in a neutral solvent containing trimethylchlorosilane under mild reaction conditions.

Scheme I



A typical procedure is described as follows. A solution of 10 g (0.33 mol) of tetraethylammonium *p*-toluenesulfonate (Et<sub>4</sub>NOTs) in 80 ml of *N,N*-dimethylformamide (DMF) was placed in cathodic (70 ml) and anodic (20 ml) chambers of a cell equipped with a lead cathode, a carbon rod anode, and a ceramic diaphragm. To the catholyte was added 0.86 g (0.01 mol) of methyl acrylate, 5.7 g (0.05 mol) of 2-heptanone, and 5.4 g (0.05 mol) of trimethylchlorosilane. The catholyte was stirred with a magnetic bar and electrochemically reduced at a constant current (200 mA/hr, 0.004 A/cm<sup>2</sup>) under external cooling with a water bath until 6 F/mol of electricity was passed. The catholyte was then poured into 200 ml of 1N HCl solution and it was extracted by three 100 ml portions of ether after stirred for about an hour. The combined ethereal solution was dried over anhydrous magnesium sulfate and evaporated. The product, 4-methyl- $\gamma$ -nonylactone,<sup>6</sup> was isolated in a 76% yield by distillation.

The wide generality of this electrochemical crossed coupling is clearly shown in the Table 1.

Table 1

Entry	$\alpha,\beta$ -Unsaturated Ester	Aldehyde or Ketone	Product <sup>a,b)</sup>	Yield, % <sup>c)</sup>
1.	$\text{CH}_2=\text{CHCOOCH}_3$	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$		73
2.		$\text{CH}_3(\text{CH}_2)_4\text{CHO}$		86
3.		$\text{CH}_3(\text{CH}_2)_6\text{CHO}$		77
4.		$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$		51
5.	$\text{CH}_3\text{CH}=\text{CHCOOCH}_3$	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$		71
6.	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$		54
7.	$\text{CH}_2=\text{C}(\text{COOCH}_3)_2$	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$		57
8.	$\text{CH}_2\text{COOCH}_3$ $\text{CH}=\text{CHCOOCH}_3$	$\text{CH}_3(\text{CH}_2)_7\text{CHO}$		59
9.	$\text{CH}_2=\text{CHCOOCH}_3$	$\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$		76
10.		$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$		67
11.				78
12.	$\text{CH}_3\text{CH}=\text{CHCOOCH}_3$	$\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$		64
13.	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	$\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$		58
14.	$\text{CH}_2=\text{C}(\text{COOCH}_3)_2$	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}_3$		86

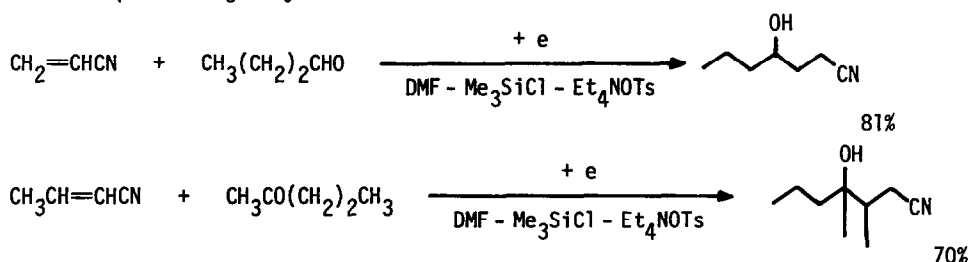
a) All products gave satisfactory spectroscopic data and elemental analysis for assigned structures. b) Products were mixtures of stereoisomers. For example, the products from methyl crotonate and butyraldehyde were a mixture of two stereoisomers in the ratio of 43:28, though the exact assignment of stereoconfiguration was not possible. c) Isolated yields.

By using this cathodic crossed hydrocoupling, a variety of  $\gamma$ -lactones which are rather difficultly obtainable by the usual chemical methods can easily be synthesized in one step from commercially available or easily accessible  $\alpha,\beta$ -unsaturated esters and carbonyl compounds.  $\gamma$ -Pelargonolactone and  $\gamma$ -undecalactone obtained through this coupling reaction are well known as key flavors of coconut and plum respectively (entry 2 and 3). Moreover, 3-carbomethoxymethyl- $\gamma$ -dodecylactone is a precursor of Avenaciolide,<sup>7</sup> which is a fungicidal bislactone (entry 8).<sup>8,9</sup>

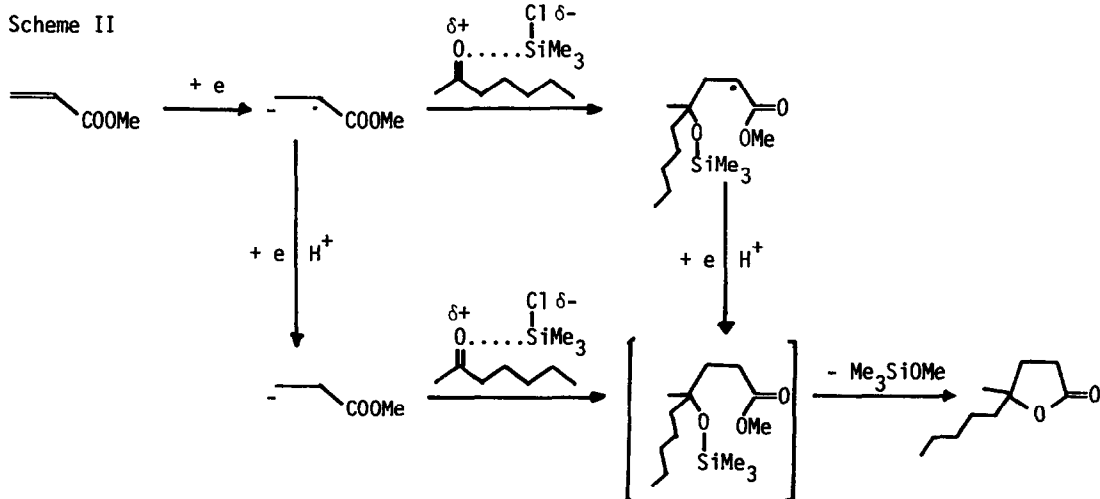
This reaction, however, did not give any coupled product when benzaldehyde, acetophenone, or benzophenone was used as the carbonyl compound.

Using  $\alpha,\beta$ -unsaturated carboxylic acids instead of their esters brought about a considerable decrease in the yields. For instance, cathodic crossed hydrocoupling of acrylic acid with butyraldehyde and with 2-heptanone gave  $\gamma$ -heptyllactone (38%) and 4-methyl- $\gamma$ -nonyllactone (32%) respectively.

Under the same reaction conditions, the coupling of  $\alpha,\beta$ -unsaturated nitriles with some carbonyl compounds took place in good yields.



The presence of trimethylchlorosilane in the reaction system is essential, because this coupling did not proceed at all in the absence of trimethylchlorosilane. Although the detail of the role of trimethylchlorosilane in this coupling still remains unexplained, the reaction may be depicted as shown in the following scheme.



In this reaction scheme, the role of trimethylchlorosilane may be the activation of carbonyl compounds as electrophiles by coordinating to carbonyl groups. The initiation of reaction<sup>10</sup> is one electron reduction of acrylic esters to anion radicals, whereas the second step is not yet clear. One possible route is coupling of the anion radicals with carbonyl compounds activated by trimethylchlorosilane, while another route is protonation of the anion radicals to radicals and further reduction of the radicals to anions.

Regardless of some ambiguity in reaction mechanism, this cathodic crossed hydrocoupling is the first reaction which shows that trimethylchlorosilane is a very effective promotor in electroreduction.<sup>11</sup>

#### References and Notes

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6. Bp 97 °C/5 mmHg; NMR (CCl<sub>4</sub>) δ 0.90 (t, 3H, CH<sub>3</sub>-, *J* = 7 Hz), 1.10 - 1.60 (m, 8H, -CH<sub>2</sub>-), 1.30 (s, 3H, CH<sub>3</sub>-), 1.98 (d, 2H, -CH<sub>2</sub>-, *J* = 7 Hz), 2.36 (d, 2H, -CH<sub>2</sub>CO-, *J* = 7 Hz); IR (neat) 1760 (C=O), 1260, 1200, 1160, 1140, 950, 930 cm<sup>-1</sup>; MS *m/e* 170 (M<sup>+</sup>). Anal. Calcd for C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>: C, 70.54; H, 10.66. Found: C, 70.23; H, 10.58.
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10. Reduction peak potentials of methyl acrylate, butyraldehyde, and 2-heptanone are - 2.16, - 2.24, and - 2.68 V vs. SCE respectively, while trimethylchlorosilane did not show any reduction peak potential between 0 ~ - 3.0 V vs. SCE [DMF-Et<sub>4</sub>NOTs (0.1 M), scanning rate 100 mV/sec, concentration of substrate 5 × 10<sup>-3</sup> M]. The addition of trimethylchlorosilane to solution of the carbonyl compounds did not bring about any shift in the reduction peak potentials of the carbonyl compounds.
11. This work has been described at the 36th Symposium on the Synthetic Organic Chemistry, Tokyo, Japan, November, 1979. An investigation based on the similar idea was reported in the next year of the above meeting. S. Torii, T. Inokuchi, and N. Hasegawa, *Chem. Lett.*, **1980**, 639.

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