CHEMISTRY LETTERS, pp. 621-624, 1975. Published by the Chemical Society of Japan

ELECTROCHEMICAL OXIDATION OF LITHIUM ESTER ENOLATES

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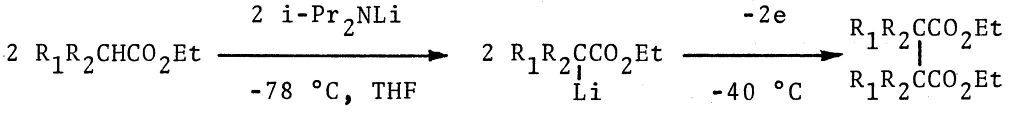
Electrochemical oxidation of lithium enolates of esters containing no activating groups at low temperature produced the corresponding substituted succinate esters in fairly good yields. Electrolysis of enolate of ethyl phenylacetate also produced a quantitative yield of the oxidative dimer with 100% current efficiency.

Although the electrochemical oxidations of ester enolates have been investigated by several workers,$^{1)}$ these studies were limited to those of esters activated by electron-withdrawing groups such as carbonyl, alkoxycarbonyl or cyano. Moreover, the products resulting from these esters were often complicated when methanol or ethanol was used as a solvent,$^{2)}$ and the yields of the oxidative dimers were generally low.$^{1,2)}$ We now wish to report a successful conversion of lithium enolate of ester containing no activating groups to its oxidative dimer by the electrochemical oxidation.

Lithium enolate of aliphatic ester (II) is readily prepared by treatment with lithium diisopropylamide in THF at -78 °C.$^{3)}$ Electrolysis of these enolates at low temperature produced the corresponding succinate esters (III)$^{4)}$ in fairly good yields. The results are summarized in Table 1.



$$2\ R_1R_2CHCO_2Et \xrightarrow[-78\ ^\circ C,\ THF]{2\ i\text{-}Pr_2NLi} 2\ R_1R_2\underset{\displaystyle Li}{\underset{|}{C}}CO_2Et \xrightarrow[-40\ ^\circ C]{-2e} \begin{array}{c}R_1R_2CCO_2Et\\ |\\ R_1R_2CCO_2Et\end{array}$$

Ia-g II III

Electrolysis was carried out at a constant current using a conventional undivided cell, with a platinum plate (1x1 cm^2) as an anode and a mercury pool as a cathode. The amount of electricity passed was equivalent to that of the ester enolate.

Table 1. Synthesis of substituted succinate esters by electrochemical oxidation

	Ester (I)		Yield of III (%)$^{a)}$		
	R_1	R_2	A$^{b)}$	B$^{c)}$	C$^{d)}$
Ia	CH_3	H	0	10	8
Ib	C_2H_5	H	0	44	41
Ic	CH_3	CH_3	trace	37	82
Id	C_4H_9	H	0	45	45
Ie	i-C_3H_7	H	—	6	—
If	-$(CH_2)_5$-		—	8	35
Ig	C_6H_5	H	100	100	100

a) Yields are based upon ester enolate employed.

b) Method A: Electrolyzed at -40 °C using Pt anode and Pt cathode in THF and HMPA; Conc. 0.2 mol/l; Current density 0.1 A/cm^2.

c) Method B: Electrolyzed at -20~-30 °C using Pt anode and Hg cathode in THF and DME; Conc. 0.4~0.6 mol/l; Current density 0.1 A/cm^2.

d) Method C: Electrolyzed at -40 °C using Pt anode and Hg cathode in THF and HMPA; Conc. 0.2 mol/l; Current density 0.1 A/cm^2.

When ester enolates were electrolyzed in THF and HMPA at -40 °C using a platinum anode and a platinum cathode (method A), the current was gradually decreased to 0 because of a covering on a cathodic surface, except that ethyl phenylacetate (Ig) produced IIIg in a quantitative yield. This difficulty was overcome by employing a mercury pool as a cathode (method B). Furthermore, when HMPA was added to THF solution in amounts equimolar with the enolate (method C), the yields of oxidative dimers were increased. Effects of reaction temperature, concentration of ester enolate and current density on the electrochemical oxidation of enolate of ethyl isobutyrate are summarized in Table 2. The electrolysis at higher temperature resulted in a decrease of the yield of the oxidative dimer and an increase of the conversion, probably because of the self-condensation reaction of ester enolate. Similar results were obtained in the electrochemical oxidation of ethyl phenylacetate. An increasing concentration of lithium enolate resulted in a lower yield of IIIc. It was confirmed that the yield of IIIc was not increased when more than one equivalent of electricity was applied to the reaction mixture.

Table 2. Electrochemical oxidation of lithium enolate of ethyl isobutyrate[a)]

Conc. (mol/l)	Temperature (°C)	Current density[b)] (A/cm^2)	Yield[d)] of IIIc (%)	Conversion[d)] of Ic (%)
0.5	-30~-40	0.1	52	78
0.5	-20~-30	0.1	43	84
0.5	0	0.1	26	93
0.35	-40	0.1	71	93
0.25	-40	0.1	82	93
0.5	-40	0.05	47	74
0.5	-40	0.1[c)]	50	98

a) Electrolyzed using Pt anode and Hg cathode in THF and HMPA.

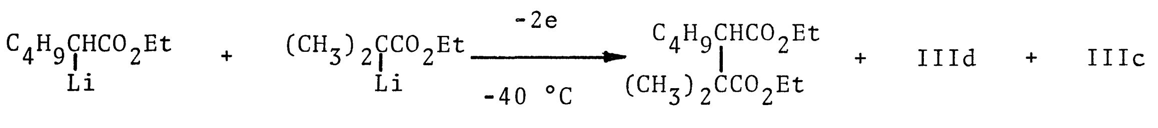
b) Amount of electricity passed: 1 F/mol.

c) Amount of electricity passed: 1.5 F/mol.

d) Based upon ester enolate employed.

Although the electrochemical oxidation of ethyl phenylacetate (Ig) by a previously reported method produced a lower yield of IIIg,[1c)] the present method produced a quantitative yield of IIIg with 100% current efficiecy. The oxidative dimers of ethyl isobutyrate (Ic) and ethyl cyclohexanecarboxylate (If) were also produced in 82 and 35% yields, respectively. A similar oxidative dimerization of ester enolate using copper (II) salts was recently reported by Rathke et al.,[5)] but their method was not satisfactory for that of substituted aliphatic ester such as isobutyrate and isovalerate esters.

Crossed coupling reaction between different lithium enolates also occurred. When a mixture of lithium enolates of ethyl hexanoate (Id) and ethyl isobutyrate (Ic) in a molar ratio of 3 to 1 was electrolyzed at -40 °C in THF and HMPA (method C), the crossed coupling product, diethyl α-butyl-α',α'-dimethylsuccinate (IIIcd), was obtained in a 48% yield, based upon IIc employed.



$$C_4H_9\underset{\displaystyle Li}{\underset{|}{C}}HCO_2Et + (CH_3)_2\underset{\displaystyle Li}{\underset{|}{C}}CO_2Et \xrightarrow[-40\ ^\circ C]{-2e} \begin{array}{l} C_4H_9CHCO_2Et \\ \qquad\ | \\ (CH_3)_2CCO_2Et \end{array} + IIId + IIIc$$

IId IIc IIIcd

This electrochemical reaction probably proceeds *via* one electron oxidation of ester enolate which was followed by a coupling of the resulting radical. It was clarified from the results that the electrolysis using a divided cell produced the oxidative dimer (III) only in the anode chamber, and an equivalent amount of electricity was sufficient for a quantitative conversion of ethyl phenylacetate to its oxidative dimer.

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(Received March 31, 1975)