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ELECTROOXIDATIVE DESULFENYLATION OF MICHAEL-TYPE THIOL ADDUCTS OF α,β-UNSATURATED ESTERS, KETONES, AND NITRILES

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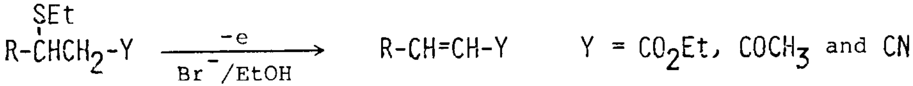
Summary Michael adducts of ethanethiol with α,β-unsaturated esters, ketones, and nitriles are conveniently desulfenylated under neutral conditions by an electrooxidation involving bromonium ion mediation.

Electrooxidative cleavage of C-S bonds serves as a new means for various synthetic reactions.1) t-Butyl thiolesters can be deprotected electrooxidatively to carboxylic acids under neutral conditions.2) We wish to report that Michael-type thiol adducts of α,β-unsaturated esters, ketones, and nitriles are readily desulfenylated by an indirect electrooxidation using bromide ion as elctrolytes.



$$\underset{\mathbf{1}}{\text{R-}\overset{\text{SEt}}{\text{C}}\text{HCH}_2\text{-Y}} \xrightarrow[\text{Br}^-/\text{EtOH}]{-e} \underset{\mathbf{2}}{\text{R-CH=CH-Y}} \qquad \text{Y} = \text{CO}_2\text{Et, COCH}_3 \text{ and CN}$$

Experimentally, a solution of **1** (5 mmol) in ethanol (25 ml) containing tetrabutylammonium bromide (2 mmol) as a supporting electrolyte was electrolyzed at a constant current of 0.2 A using platinum electrodes in an undivided cell until over 95% of **1** was consumed. The electrolysate was extracted with hexane; usual work-up gave **2** and its yields were determined by GLC (Table).

The desulfenylation of **1** took place smoothly in methanol, ethanol, and aqueous acetonitrile in comparable yields. The effect of thiol substituents (Me, t-Bu, and Ph in place of Et in **1**) on the yield of **2** is relatively small. These alkylthio and phenylthio residues cleaved from **1** were oxidized mostly into the corresponding sulfinates. Halide electrolytes such as Bu_4NCl, LiBr, and Bu_4NBr caused high yields of **2**, whereas others including ClO_4^- or BF_4^- ion gave poor results. Cyclic voltammetric study showed that Cl^- and Br^- discharged at *ca.* +1.3 and 1.1 V vs Ag/AgCl, respectively, and these potentials were much

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Table Electrooxidative Desulfenylation

1	Solvent	F/mol[a]	Yield of **2**,%
$CH_3CH(SEt)CH_2CO_2Et$	EtOH	3.7	98 (100/0)[c]
$CH_3CH(SEt)CH_2CO_2Me$	EtOH[b]	4.0	90 (100/0)[c]
$PhCH(SEt)CH_2CO_2Et$	EtOH	3.3	24 (100/0)[c]
$BuO_2CCH(CH_2SEt)CH_2CO_2Bu$	EtOH[b]	3.7	58
$(CH_3)_2C(SEt)CH_2COCH_3$	EtOH	2.2	73
$PhCH(SEt)CH_2COCH_3$	MeOH	3.0	24 (100/0)[c]
$CH_3CH(SEt)CH_2CN$	MeOH	4.0	67[d] (48/52)[c]
$CH_3(CH_2)_2CH(SEt)CH_2CN$	MeOH	3.0	78 (46/54)[c]
$CH_3CH(SEt)CH(CH_3)CN$	MeOH	3.0	28 (33/67)[c]

a) Electricity passed. b) Coelectrolyte NH_4Cl (2 mmol) was added to suppress the ester exchange reactions. c) E/Z ratio. d) LiBr electrolyte gave 79% yield.

lower than those of **1** (+1.9 V for Y = CO_2Et and 2.2 V for Y = CN). As the amount of bromide ion used under this experimental condition was only 0.4 equivalent to **1**, the present desulfenylation is apparently mediated by bromide ion, which is oxidized initially to bromonium ion[3)] capable of attack on sulfur atoms in **1**.

From the Table, simple β-alkyl substituted esters, ketones and nitriles are shown to give good yields of desulfenylated olefins. β-Phenyl substituted ester and ketone give rise to unfavorable hydrogenation products and hydrodimers due to the cathodic reductions of **2**. α,β-Unsaturated nitriles produced were a mixture of E and Z isomers, identical to thermodynamically equilibrated ones.

The present electrooxidative desulfenylation can be performed by a simple procedure under neutral conditions, and therefore useful for the synthesis and protection of α,β-unsaturated compounds.[4,5)] A related mechanistic study is in progress.

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