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ELECTROCHEMICAL SYNTHESIS OF ALDEHYDES AND ACETALS FROM α-PHENYLTHIOCARBOXYLIC ACID

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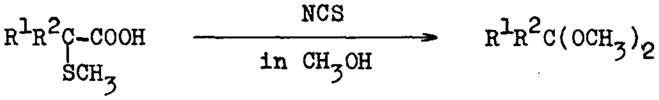
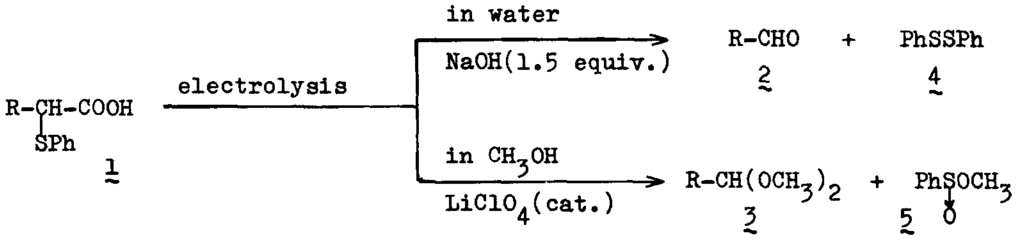
Summary: α-Phenylthiocarboxylic acids were converted to the corresponding aldehydes or acetals with oxidative decarboxylation and desulfurization by electrolysis.

Organosulfur compounds which can function as key intermediates have been widely used in organic synthesis. The desulfurization of these compounds has been considered to be the most important and interesting step of the synthetic process. In recent years, Trost et al. have reported the oxidative decarboxylation of α-methylthiocarboxylic acids associated with desulfurization to give the corresponding ketals or acetals by using N-chlorosuccinimide(NCS) in methanol.$^{1)}$



$$R^1R^2\underset{SCH_3}{C}\text{-COOH} \xrightarrow[\text{in } CH_3OH]{\text{NCS}} R^1R^2C(OCH_3)_2$$

Now, we have found that the reaction similar to that described above proceeds by electrolysis of α-phenylthioalkanoic acids under mild conditions without using oxidizing agents as shown below.$^{2)}$



The α-phenylthiocarboxylic acid(**1**) can be obtained easily by the sulfenylation of carboxylic acid (or α-halocarboxylic acid) or by the alkylation of α-phenylthioacetic acid.3) The results of this decarboxylation reaction associated with desulfurization are summarized in Table 1.

Table 1 The yields of aldehydes(**2**) and acetals(**3**).

	1	**2** Yield(%)	**3** Yield(%)
(a)	R= $CH_3(CH_2)_3$	48	72
(b)	$CH_3(CH_2)_5$	75	93
(c)	$CH_3(CH_2)_7$	91	95
(d)	$C_2H_5O_2C(CH_2)_3$	-	79
(e)	$C_4H_9O_2C(CH_2)_3$	trace	90
(f)	$C_4H_9O_2C(CH_2)_{13}$	35	98

A typical procedure of the conversion of **1** *to* **2** *and* **3** *is as follows.* Electrolysis of α-phenylthiodecanoic acid(**1c**)(2 mmol) in water(20 ml) with sodium hydroxide(3 mmol) and hexane(15 x 4 ml)4) using platinum electrodes(3 cm^2, immersed in water layer) at an initial current density 0.04 A/cm^2, applied voltage ca. 8 V, for 4 hours(9 F/mol) at 25°C afforded nonanal(**2c**)(91%), diphenyldisulfide(90 mg) and paraffinic impurity(32 mg). Similarly, electrolysis in methanol(30 ml) with lithium perchlorate(50 mg), at an initial current density 0.04 A/cm^2, applied voltage ca. 9 V, for 7 hours(12 F/mol) at 25-8°C gave 1,1-dimethoxynonane(**3c**)(95%) with methyl sulfinate(**5**)(30%).

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References and Notes

1) B. M. Trost and Y. Tamaru, J. Amer. Chem. Soc., **99**, 3101(1977).
2) Electrolytic ketalization of α-(arylthio)diphenylacetic acids has been reported: B. Wladislaw, Chem. Ind. (London), 1868(1962).
3) Ref. 1); S. N. Lewis, J. J. Miller, and S. Winstein, J. Org. Chem., **37**, 1478 (1972).
4) Hexane(15 ml, upper layer) should be replaced by fresh solvent at least every hour. The combined hexane(ca. 60 ml) fraction were dried; removal of the hexane under reduced pressure gave the mixture of the products.

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