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A NOVEL ELECTROSYNTHESIS OF α,α-DIMETHOXYALKANOATES FROM α-(2-BENZOTHIAZOLYLTHIO)ALKANOATES

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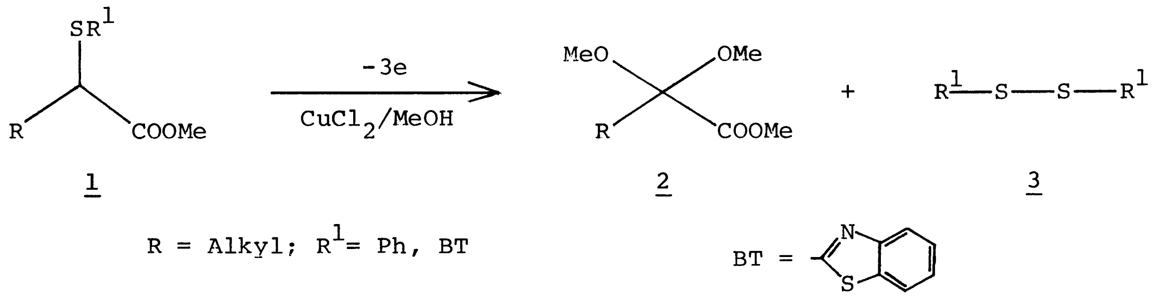
An efficient preparation of α,α-dimethoxyalkanoates (2) has been performed by electrolytic desulfurization of α-(2-benzothiazolylthio)alkanoates (1) in MeOH containing $CuCl_2$ as a catalytic additive, yielding 2 (94-57%) together with disulfide 3 (88-48%).

In our preceding papers, we reported a convenient synthesis of α-(2-benzothiazolylthio)alkanoates [1, R^1= 2-benzothiazolyl (BT)]$^{1)}$ along with the electrolytic desulfurization of 1, providing efficient routes to ketones$^{2)}$ and α-substituted alkanoates.$^{3)}$ As an extention work, we described here a straightforward electrosynthesis of α,α-dimethoxyalkanoates (2)$^{4)}$ from 1 (R^1 = BT, Ph) as shown below.



R = Alkyl; R^1= Ph, BT

A typical electrolysis procedure is as follows: a solution of 1 (R = C_6H_{13}, R^1= BT; 0.33 mmol) in MeOH (10 ml) containing Et_4NClO_4 (TEAP, 100 mg) and $CuCl_2$ (6 mg) was placed in a cell fitted with two platinum foil electrodes (1.5 × 2 cm^2). Electrolysis was carried out under a constant current of 13.3 mA/cm^2, 4.5-4.8 V, changing the current direction every 30 sec, at room temperature. After 11 F/mol of electricity were passed (2.4 h), yellow precipitates were collected by filtration and washed with MeOH, yielding disulfide 3 (R^1= BT; 80%).$^{5)}$ The filtrates were concentrated in vacuo and the residue was taken up in ether, washed with brine, and dried (Na_2SO_4). Evaporation of the solvent followed by column chromatography gave 2$^{6)}$ (83%).

Table Electrosynthesis of α,α-Dimethoxyalkanoates (2)

Entry	α-Sulfenylalkanoates 1		Electrolyte	Product, yield %$^{a)}$	
	R	R^1		Acetal 2	BT-SS-BT 3
1	C_6H_{13}	BT	TAEP	83 (61)	80 (—)
2	"	"	H_2SO_4	94 (53)	58 (—)
3	"	"	Et_3N	—	—$^{b)}$
4	"	Ph	TEAP	68	$59^{c)}$
5	Me_2CHCH_2	BT	"	76	77
6	"	"	H_2SO_4	70	52
7	$MeOCO(CH_2)_3$	"	TEAP	57	88
8	"	"	H_2SO_4	62	58
9	$MeOCH_2CH_2$	"	TEAP	70	83
10	$PhCH_2$	"	H_2SO_4	63	48

a) Isolated yields; number in parenthesis is a yield provided by electrolysis without adding $CuCl_2$. b) 1 (78%) was recovered. c) $PhSO_2Me$; see ref. 7.

As shown in Table, the same electrolytic acetalization took place in MeOH (10 ml)-H_2SO_4 (0.02 ml), in contrast to the result obtained in basic media (entry 3). It is interesting to note that the presence of $CuCl_2$ in the electrolysis media is fruitful. The absence of $CuCl_2$ brought about not only considerable decrease of the yields of the acetal 2, but also difficulties in recovering disulfide 3.

The reaction mechanism along with the role of $CuCl_2$ will be discussed elsewhere.

References and Notes

1) S. Torii, H. Tanaka, and H. Okumoto, Bull. Chem. Soc. Jpn., 52, 267 (1979).

2) (a) S. Torii, H. Tanaka, Y. Kobayasi, J. Nokami, and M. Kawada, Bull. Chem. Soc. Jpn., 52, 1553 (1979); J. Nokami, M. Kawada, R. Okawara, S. Torii, and H. Tanaka, Tetrahedron Lett., 1979, 1045.

3) S. Torii, H. Okumoto, and H. Tanaka, J. Org. Chem., 45, (1980) in press.

4) The conversion of 1 (R^1= Et) to 2 on treatment with thallium trinitrate in MeOH has been reported: Y. Nagao, K. Kaneko, and E. Fujita, Tetrahedron Lett., 1978, 4115.

5) Disulfide 3 (R^1= BT) can be converted into the corresponding sulfenamides, which are the useful reagent for the preparation of 1: S. Torii, H. Tanaka, and M. Ukida, J. Org. Chem., 43, 3223 (1978); see also ref. 1.

6) All new compounds indicate the reasonable IR, ^1H NMR, and analytical data.

7) J. Nokami, Y. Fujita, and R. Okawara, Tetrahedron Lett., 1979, 3659.

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