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STEREOSELECTIVE ELECTROOXIDATION OF A THIANE TO THE CORRESPONDING THIANE OXIDE

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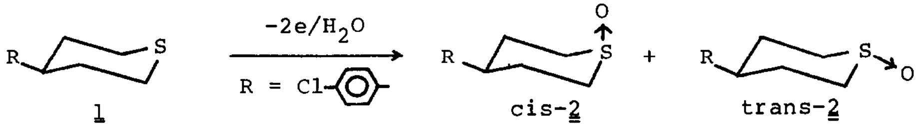
Summary: Electrochemical oxidation of 4-(p-chlorophenyl)thiane in aqueous organic solvents gave selectively the trans-sulfoxide by bromonium ion mediation. A preferential formation of the cis-sulfoxide was attained under acidic electrolyses.

Electrolyses in the presence of halide salts as electrolytes produce halonium ions such as chloronium,1) bromonium,2) and iodonium ion3) leading to valuable synthetic potentialities. Shono et al.2a) have developed a double mediatory system for the oxidation of alcohols, where bromonium ion Br^+ generated electrochemically reacts with sulfides to yield bromosulfonium intermediates R_2S^+Br4) responsible for the oxidation.

Cis and trans stereoselectivities in the oxidation of cyclic sulfides to sulfoxides have been studied with a variety of oxidants including positive halogen compounds.5) Of the two extreme cases in 4-(p-chlorophenyl)thianes (1), t-butyl hypochlorite in MeOH exerts the highest cis selectivity (cis/trans = 98/2 at -78°),6) while benzeneiodonium dichloride in aqueous pyridine shows high trans selectivity (cis/trans = 5/95 at -40°).7) However, little has been



1 cis-2 trans-2

elucidated on the stereochemical features in the electrooxidation of sulfides to sulfoxides.[8)] We have found that electrooxidation of 1 shows a good cis or trans selectivity depending on solvents, electrolytes and water contents etc.

Typically, a solution of 1 (0.25 mmol) and tetrabutylammonium bromide (2.5 mmol) in an aqueous (10% H_2O) organic solvent (25 mL) was electrolyzed at constant voltage of +1.4 V vs. Ag/AgCl[9)] in an undivided cell using Pt electrodes by passing ∿2 F/mol of current. A mixture of cis- and trans-sulfoxides (2) was obtained and their ratio was determined by HPLC (Table 1). High yields (>80%) of 2 were obtained with various bromide salts as electrolytes, while chloride salts were less sufficient because of contamination with chlorinated sulfoxides and sulfone. Only poor reactivity was observed with electrolytes such as NaI, KF, $LiNO_3$, Et_4NOTs, and Bu_4NClO_4. Since Br^- and Cl^- discharge at the lower potential (ca. +1.0 and +1.3 V in aqueous solvents, respectively) than 1,[9)] the present oxidation clearly proceeds via an indirect pathway involving halonium ions to give R_2S^+Br and R_2S^+Cl.[10)] The cis/trans ratios of 2 (Table 1) show that the present oxidation possesses high trans selectivity with small dependence on solvents. Some of trans selectivities obtained are close to the highest one reported with $PhICl_2$ (cis/trans = 10/90 at 25°).[7,11)] Since equilibrated mixtures of 2 are composed of 80% of cis-2 and 20% of trans-2,[6)] this electrooxidation is kinetically controlled.

Table 1. Cis : trans Ratio of 2 in Electrolysis of 1.

Electrolyte	Solvent[a)]	cis : trans
Bu_4NBr	MeCN	9 : 91
	Dioxane	7 : 93
	THF	23 : 77
	AcOH	8 : 92
	MeOH	20 : 80
	t-BuOH-CH_2Cl_2	9 : 91
LiBr	MeCN	20 : 80
$MgBr_2$	MeCN	17 : 83
Bu_4NCl	Dioxane	9 : 91[b]
LiCl	MeCN	30 : 70[b]

a) Aqueous solvent containing 10 vol.% water. b) Yield of 2 was as low as ca. 50%.

Table 2. Effect of Water Contents on the cis : trans Ratio of 2.[a)]

Solvent	H_2O (%)	cis : trans
MeCN	0.25	no react
	0.5	46 : 54
	1.0	37 : 63
	4.0	18 : 82
	10	9 : 91
$Me_2C=O$	1.0	31 : 69
	10	19 : 81

a) Electrolysis of 0.01 M 1 with 0.1 M Bu_4NBr

The cis/trans ratios were found to vary with water contents in solvents. The effect was significant in the case of weak donor solvents such as MeCN and $Me_2C=O$ (Table 2), but not conspicuous for strong donor solvents (dioxane, THF)[12)] or hydroxylic solvents (MeOH, t-BuOH, AcOH). An increase in the water content results in the increase of trans selectivity. In contrast, the ratios were little dependent on the electrolyte concentration under various water contents and solvents; e.g., a wide variation in the concentration of Bu_4NBr (0.1 - 0.0025 M) resulted in a relatively small change in the cis/trans ratio (9/91 - 19/81 in $MeCN-H_2O$ (9/1)).

In order to obtain a higher cis selectivity, several attempts have been carried out. Electrolyses of 1 in the presence of sulfuric acid encountered preferential formations of cis-2; e.g., a run with Bu_4NBr (0.01 M), 0.5% water, and H_2SO_4 (0.03 M) in MeCN gave cis/trans of 67/33. Since the H_2SO_4-catalyzed isomerization of trans-2 to cis-2 was negligibly slow under the reaction conditions, the effect of H_2SO_4 may exert on the formation and/or hydrolysis of R_2S^+Br. Electrolyses of 1 at constant +2.0 V in the presence of oxygen in non-aqueous solutions gave also mixtures of 2 with lower stereoselectivity, probably reflecting a direct oxidation from cation radical of 1; runs in MeCN solutions containing Bu_4NBr or Bu_4NBF_4 under oxygen bubbling resulted in 39/61 or 59/41 of cis/trans ratio, respectively.

The present electrochemical methods illustrate a possibility of cis or trans selective oxidation of cyclic sulfides to sulfoxides, and will be of use in stereoselective syntheses of sulfoxide amino acids such as naturally occurring chondrine and cycloalliin.13) Studies on the detailed mechanism of these electrooxidations are currently in progress.

References and Notes

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