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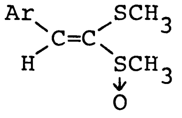
ELECTROLYTIC REDUCTION OF 1-METHYLSULFINYL-1-METYLTHIO-2-ARYLETHENES AT MERCURY AND PLATINUM ELECTRODES IN ACETONITRILE

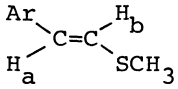
Akira KUNUGI* and Kyo ABE[†]
Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558
[†] Department of Chemistry, Faculty of Science, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558

The electrolytic reduction of 1-methylsulfinyl-1-methylthio-2-arylethenes involves a cleavage of one carbon-sulfur bond, resulting in formation of E-1-methylthio-2-arylethenes in good yields, but not Z-isomers, in the presence of excess phenol as a proton donor.

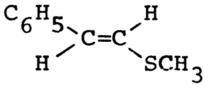
Recently, organic syntheses using methyl methylthiomethyl sulfoxide (FAMSO) have been reported.[1)] 1-Methylsulfinyl-1-methylthio-2-arylethenes (1), prepared by the condensation of FAMSO with aromatic aldehydes, are reduced with lithium aluminium hydride to afford arylacetaldehyde dimethylmercaptols,[2)] while Z-1-methylthio-2-arylethenes (Z-2) are isolated by the reduction with butyllithium.[3)] In this letter, we wish to report the electrolytic reduction of 1 at mercury and platinum electrodes in anhydrous acetonitrile, where desulfinylated compounds, E-1-methylthio-2-arylethenes (E-2) are obtained in good yields, in the presence of excess phenol. The substrates 1 and the related compounds investigated in this work are as follows.



1



E-2



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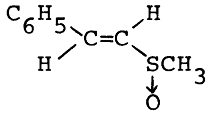


4

1 and E-2
a: Ar=C_6H_5
b: Ar=p-CH_3O-C_6H_4
c: Ar=m-CH_3O-C_6H_4
d: Ar=p-F-C_6H_4

Controlled potential macroelectrolysis and coulometry were conducted in a three-compartment cell with a mercury pool or a platinum plate as a working electrode (about 6 cm^2) at 27 °C. The reference compartment contained a silver/0.1 M silver nitrate in acetonitrile reference electrode (1 M = 1 mol dm^{-3}) and the counter compartment contained a platinum gauze. All the potentials cited here are referred to this reference electrode. These compartments were separated from the working electrode compartment with a plug of glass frit. Typical procedure for the electrolytic reduction of 1 is as follows. Anhydrous acetonitrile (25 cm^3) containing 0.1 M tetrabutylammonium tetrafluoroborate was pipetted into the working electrode compartment and suitable amounts of the same solution were added to the counter and reference compartments. The solution was deaerated with nitrogen for 0.5 h and then was pre-electrolyzed at a potential somewhat more negative than that at which the electrolysis was to be run. Then, weighed amounts of the arylethene (0.20-0.25 g) and phenol (0.36-0.42 g) were added to the working electrode compartment and after further deaeration, controlled potential electrolysis at -2.3 V[4)] was carried out. After the electrolytic reduction was virtually completed, the reaction mixture was worked up to give the desulfinylated compound in good yields.

In Table 1 are presented the yields of the isolated desulfinylated compounds, E-2a – E-2d,[5)] produced by the electrolyses of 1a – 1d, respectively, with the coulometric n-values. The yields of E-2a – E-2d were very high in the presence of phenol, whereas they were low in the absence of proton donors. The stereochemical structure of E-2a – E-2d was determined on the basis of the NMR spectra of their olefinic protons (H_a and H_b). The NMR spectra of H_a and H_b exhibited the AB quartet splitting with J = 15.3 Hz in every case (cf., for Z-2a, ABq J = 10.45 Hz[3)]). Perusal of the NMR spectra of the reaction mixture indicated that Z-isomers were not produced in every experiment. The data in Table 1 show that, with regard to the yields and the n-values, the electrolytic reduction of 1a – 1d is independent of the nature of the electrode material. Interestingly there is a sharp difference between the electrolytic and non-electrolytic methods in the reduction of 1: the electrolytic desulfinylation gives the E-2 isomers whereas the reduction with butyllithium gives the Z-2 isomers.

Dc polarography of 1a – 1d and related compounds such as 1,1-dimethylthio-2-phenylethene (3), 1-methylsulfinyl-2-phenylethene (4), and 2a was carried out in anhydrous acetonitrile containing 0.1 M tetrabutylammonium perchlorate and phenol

Table 1. Controlled potential electrolyses of 1a – 1d at -2.3 V[a)] in CH_3CN containing 0.1 M Bu_4NBF_4

Substrate	Cathode material	Phenol/substrate initial molar ratio	Coulometric n-value[b)]	Product	Yield %
1a	Hg	0	1.0	E-2a	6
1a	Pt	0	1.0	E-2a	7
1a	Hg	4.1	3.6	E-2a	85
1a	Pt	4.2	3.6	E-2a	86
1b	Hg	4.1	3.5	E-2b	87
1c	Hg	4.5	3.6	E-2c	73
1d	Hg	4.5	3.5	E-2d	79

a) Against Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode.

b) Coulometric n-values, electrons per molecule of the substrate, were calculated from the quantity of electricity passed and the amount of substrate added.

(4 times the concentration of the substrate). The half-wave potentials of the first wave ($E_{1/2}$) are summerized in Table 2. The half-wave potential of 3 suggests that it cannot be an intermediate of the electrolytic reduction of 1a to E-2a at -2.3 V. In fact, 3 was not detected in this reduction. On the other hand, evidently 4 is reduced electrochemically at -2.3 V (Table 2). However, 4 also is not thought to be an intermediate in the reductive conversion of 1a to E-2a, because the controlled potential electrolysis of 4 at -2.5 V in the presence of

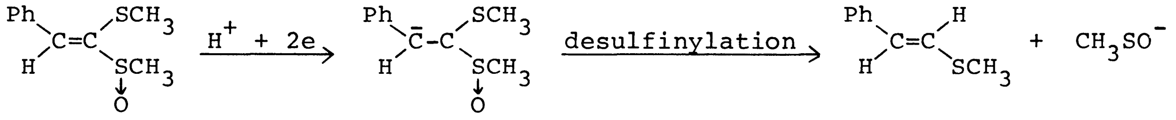
Table 2. Values of $E_{1/2}$ for the first reduction wave of 1a – 1d and the related compounds in CH_3CN containing 0.1 M Bu_4NClO_4 in the presence of excess phenol[a)]

Substrate	$E_{1/2}$ /V[b)]	Substrate	$E_{1/2}$ /V[b)]
1a	-2.16	E-2a	-2.81
1b	-2.17	3	-2.51
1c	-2.17	4	-2.31
1d	-2.16		

a) Concentrations of substrates and phenol were 1.0-1.3 mM and 4 times that of the substrate, respectively.

b) Against Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode, at 27 °C.

excess phenol afforded E-2a in 10% yield. Furthermore, the polarographic wave corresponding to the reduction of 4 was not observed in both dc and differential pulse polarograms of 1a. It follows that the electrolytic reduction of 1a to E-2a does not proceed via 3 and 4, but via the electrochemical desulfinylation:



1a E-2a

The other substrates, 1b, 1c, and 1d, exhibited the same polarographic behavior as did 1a, and the results of the controlled potential electrolyses of 1b, 1c, and 1d were the same as those of 1a (Table 1). Therefore, the electrolytic reduction of 1b, 1c, and 1d also will proceed according to the above scheme. Methylsulfinyl anion (CH_3SO^-) generated during the controlled potential electrolyses of 1a – 1d will further undergo electrochemical reduction to yield probably methanethiol, since the coulometric n-values for 1a – 1d in the presence of excess phenol were 3.5-3.6 and the characteristic odor like methanethiol was detected during the course of the controlled potential electrolyses of 1a – 1d.

References

1) K. Ogura, Yuki Gosei Kagaku, 37, 903 (1979).
2) K. Ogura and G. Tsuchihashi, Tetrahedron Lett., 1972, 1383.
3) K. Abe, H. Nakata, Y. Kishimoto, N. Nakamura, and A. Fujino, J. Chem. Soc., Chem. Commun., submitted.
4) This potential corresponds to the first polarographic wave for 1a – 1d.
5) The chemical shifts for ^1H NMR are given in δ ppm downfield from internal tetramethylsilane.

E-2a: NMR($CDCl_3$) δ 2.32(3H, s, $-SCH_3$), 6.22(1H, d, J=15.3 Hz, H_a), 6.66(1H, d, J=15.3 Hz, H_b), 6.96-7.28(5H, m, aromatic H).

E-2b: NMR($CDCl_3$) δ 2.32(3H, s, $-SCH_3$), 3.76(3H, s, $-OCH_3$), 6.22(1H, d, J=15.3 Hz, H_a), 6.50(1H, d, J=15.3 Hz, H_b), 6.78, 7.14(4H, dd, J=10.0 Hz, aromatic H).

E-2c: NMR($CDCl_3$) δ 2.28(3H, s, $-SCH_3$), 3.70(3H, s, $-OCH_3$), 6.16(1H, d, J=15.3 Hz, H_a), 6.62(1H, d, J=15.3 Hz, H_b), 6.40-7.26(4H, m, aromatic H).

E-2d: NMR($CDCl_3$) δ 2.32(3H, s, $-SCH_3$), 6.16(1H, d, J=15.3 Hz, H_a), 6.53(1H, d, J=15.3 Hz, H_b), 6.68-7.28(4H, m, aromatic H).

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