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

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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 ($\underline{1}$), 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-$\underline{2}$) are isolated by the reduction with butyllithium.[3] In this letter, we wish to report the electrolytic reduction of $\underline{1}$ at mercury and platinum electrodes in anhydrous acetonitrile, where desulfinylated compounds, E-1-methylthio-2-arylethenes (E-$\underline{2}$) are obtained in good yields, in the presence of excess phenol.   The substrates $\underline{1}$ and the related compounds investigated in this work are as follows.

$\underline{1}$ and E-$\underline{2}$

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
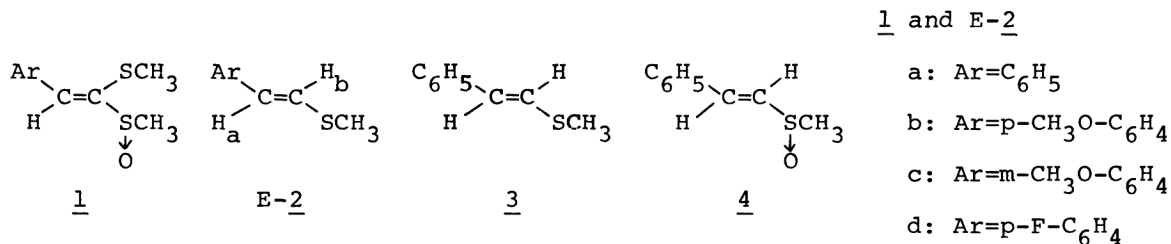
Controlled potential macroelectrolysis and coulometry were conducted in a

three-compartment cell with a mercury pool or a platinum plate as a working elec-
trode (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 ni-
trogen for 0.5 h and then was pre-electrolyzed at a potential somewhat more nega-
tive 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 electrol-
ysis 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 stereo-
chemical 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 re-
duction 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 <u>1a</u> — <u>1d</u> 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 %
<u>1a</u>	Hg	0	1.0	E-<u>2a</u>	6
<u>1a</u>	Pt	0	1.0	E-<u>2a</u>	7
<u>1a</u>	Hg	4.1	3.6	E-<u>2a</u>	85
<u>1a</u>	Pt	4.2	3.6	E-<u>2a</u>	86
<u>1b</u>	Hg	4.1	3.5	E-<u>2b</u>	87
<u>1c</u>	Hg	4.5	3.6	E-<u>2c</u>	73
<u>1d</u>	Hg	4.5	3.5	E-<u>2d</u>	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 <u>3</u> suggests that it cannot be an intermediate of the electrolytic reduction of <u>1a</u> to **E-<u>2a</u>** at -2.3 V. In fact, <u>3</u> was not detected in this reduction. On the other hand, evidently <u>4</u> is reduced electrochemically at -2.3 V (Table 2). However, <u>4</u> also is not thought to be an intermediate in the reductive conversion of <u>1a</u> to E-<u>2a</u>, because the controlled potential electrolysis of <u>4</u> at -2.5 V in the presence of
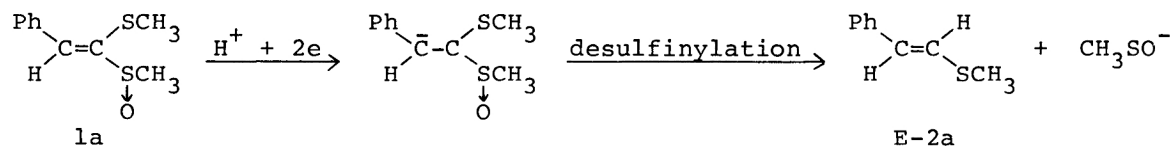
Table 2. Values of $E_{1/2}$ for the first reduction wave of <u>1a</u> — <u>1d</u> and the related compounds in CH_3CN containing 0.1 M Bu_4NClO_4 in the presence of excess phenol[a]

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

$$
\underset{\underline{1a}}{\overset{\displaystyle Ph\diagdown \atop H\diagup}{C=C}\diagup SCH_3 \atop \diagdown \underset{O}{\overset{\downarrow}{S}}CH_3} \xrightarrow{\ H^+ + 2e\ } \underset{\underline{}}{\overset{\displaystyle Ph\diagdown \atop H\diagup}{\overset{-}{C}-C}\diagup SCH_3 \atop \diagdown \underset{O}{\overset{\downarrow}{S}}CH_3} \xrightarrow{\ desulfinylation\ } \underset{E-\underline{2a}}{\overset{\displaystyle Ph\diagdown \atop H\diagup}{C=C}\diagup H \atop \diagdown SCH_3} + CH_3SO^-
$$

The other substrates, 1b, 1c, and 1d, exhibited the same polarographic behav-

ior 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 re-

duction of 1b, 1c, and 1d also will proceed according to the above scheme. Meth-

ylsulfinyl anion (CH_3SO^-) generated during the controlled potential electrolyses

of 1a − 1d will further undergo electrochemical reduction to yield probably meth-

anethiol, 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 ^{1}H 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).