Electrolytic Reduction of 1-Methylsulfinyl-1-methylthio-1-alkenes at Mercury Electrode in Nonaqueous Media

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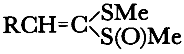
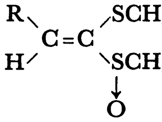
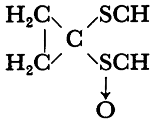
Synopsis. In the electrolytic reduction of organic sulfur compounds of general formular  $RCH{=}C{<}\begin{matrix}SMe\\S(O)Me\end{matrix}$, the substrates with R=aryl are much easier to reduce than those with R=alkyl, and the former substrates afford the desulfinylated compounds, E-isomers of RCH=CH(SMe), in good yields, but the later substrates do not give the corresponding desulfinylated compounds.

The title compounds, 1-methylsulfinyl-1-methylthio-1-alkenes (**1**), exhibit extremely interesting properties in their synthetic and mechanistic aspects.[1—5] Interestingly our preceding work[6] has shown that there is a sharp difference between the electrolytic and nonelectrolytic methods in the reduction of (*E*)-1-methylsulfinyl-1-methylthio-2-phenylethene (**1a**); the electrolytic reduction gives the desulfinylated compound, (*E*)-1-methylthio-2-phenylethene ((*E*)-**2a**), whereas the reduction with lithium aluminium hydride affords 2-phenyl-1,1-bis(methylthio)ethane.[1]

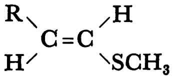
In the present work, the influence of a substituent group on the electrolytic reduction of **1** at a mercury electrode was examined in nonaqueous acetonitrile (MeCN) or *N*,*N*-dimethylformamide (DMF) containing excess phenol as a proton donor. The substrates investigated in this work are as follows.



1a—h



1i



2a—h

a : R=C_6H_5,
b : R=*p*-$CH_3OC_6H_4$
c : R=*m*-$CH_3OC_6H_4$
d : R=*p*-FC_6H_4
e : R=1-naphthyl
f : R=2-naphthyl
g : R=$(CH_3)_3C$
h : R=$HOCH_2C(CH_3)_2$

Experimental

The substrates, **1a—h**, were prepared from methyl methylthiomethyl sulfoxide (FAMSO) and the corresponding aldehydes according to the publised method[1] and **1i** was synthesized from FAMSO and 1,2-bis(tosyloxy)ethane according to a method described in the literature.[4] Verification of the substrates was made by ^1H NMR spectroscopy and by comparision of the physical properties with published values.

Nonaqueous acetonitrile solutions were prepared from predeoxygenated MeCN and tetrabutylammonium tetrafluoroborate (TBAB) or tetrabutylammonium perchlorate (TBAP) which were purified and dried as described previously.[6] Nonaqueous *N*,*N*-dimethylformamide solutions were prepared from the predeoxygenated DMF and TBAB or tetrabutylammonium iodide (TBAI). DMF was purified in a manner similar to that described in the literature.[7] TBAI was recrystallized twice from acetone and dried in vacuo at 80 °C for 3 d. The concentration of the supporting electrolyte was 0.1 mol dm^{-3}.

Controlled potential macroelectrolysis and polarography were carried out, using the same experimental set-up and procedure as reported in the previous paper.[6]

Indirect electrolysis of **1g** using phenanthrene as a mediator was carried out at the stirred mercury pool cathode of −2.8 V vs. Ag/Ag$^+$ in MeCN/TBAB without proton donor.

Results and Discussion

Polarography. d.c. Polarograms of **1a—f** in MeCN/TBAP or DMF/TBAI in the presence of excess phenol exhibited three waves. The third reduction wave is ascribed to the further reduction of the reduction products, **2a—f**, since controlled potential macroelectrolysis of **1a—f** at the plateau potential of the first wave afforded **2a—f** in high yields, respectively (vide infra). The half-wave potentials of the first reduction wave ($E_{1/2}$) of **1a—i** in MeCN/TBAP in the presence of excess phenol are summarized in Table 1, together with the results in DMF/TBAI. Among the substrates with R=substituted phenyl, **1a—d**, these $E_{1/2}$ seem to depend on the substituent constant sigma. The substrates with R=naphthyl, **1e** and **1f** were easy to reduce by 80—100 mV compared with **1a**. This can be interpreted in terms of stabilization of the le-reduction product due to the high delocalization of the charge of the radical anions of **1e** and **1f** through 1- and 2-naphthyl groups. On the other hand, the substrates with R=alkyl, **1g** and **1h**, were much more difficult to reduce than **1a**, but **1i** was not reducible in the accessible potential region.

Macroelectrolysis. Controlled potential macroelectrolyses of **1a—h** at the plateau potential of the first reduction wave at the stirred mercury pool electrode were conducted in MeCN/TBAB or DMF/TBAI in the presece of excess phenol. Table 2 summarizes the isolated yields of (*E*)-**2**, in which the coulometric *n*-values (electrons molecule^{-1}) also are included. The table shows that the substrates with R=aryl, **1a—f**, afford the desulfinylated compounds, (*E*)-**2a**-(*E*)-**2f**, in good yields, whereas the substrates with R=alkyl, **1g** and **1h**, do not give the corresponding desulfinylated compounds, **2g** and **2h**, but a complex mixture of products. The stereochemical structure of (*E*)-**2a**-(*E*)-**2f** was determined on the basis of the NMR spectra of their olefinic protons. The NMR spectra of the H exhibited

Table 1. Half-wave Potentials for the First Reduction Wave of **1a**—**i** in MeCN Containing 0.1 mol dm^{-3} TBAP and DMF Containing 0.1 mol dm^{-3} TBAI in the Presence of Excess Phenol at 27 °C[a]

Substrate	$E_{1/2}$ in MeCN/V[b]	$E_{1/2}$ in DMF/V[c]
1a	−2.16	−1.41
1b	−2.27	−1.51
1c	−2.17	−1.40
1d	−2.16	−1.42
1e	−2.08	−1.31
1f	−2.08	−1.31
1g	−2.90	
1h	−2.90	
1i	no wave	

a) Concentrations of substrates and proton donor were 1.0—1.3×10^{-3} mol dm^{-3} and 4 times that of the substrate, respectively. b) Vs. Ag/0.1 mol dm^{-3} AgNO$_3$ in MeCN reference electrode. c) Vs. Ag/AgI 0.1 mol dm^{-3} TBAI in DMF reference electrode.

Table 2. Results of Controlled Potential Electrolysis of **1a**—**h** at the First Reduction Potential at an Hg Pool Cathode in Nonaqueous Media Containing Excess Phenol

Substrate	Electrolyte system	n-Value	Yield of (E)-**2**/%
1a	MeCN/0.1 mol dm^{-3} TBAB	3.6	85
	DMF/0.1 mol dm^{-3} TBAI	3.5	78
1b	MeCN/0.1 mol dm^{-3} TBAB	3.5	87
1c	MeCN/0.1 mol dm^{-3} TBAB	3.6	73
	DMF/0.1 mol dm^{-3} TBAI	3.4	78
1d	MeCN/0.1 mol dm^{-3} TBAF	3.5	79
1e	MeCN/0.1 mol dm^{-3} TBAB	4.2	80
	DMF/0.1 mol dm^{-3} TBAI	3.6	76
1f	MeCN/0.1 mol dm^{-3} TBAB	3.9	78
	DMF/0.1 mol dm^{-3} TBAI	3.4	78
1g	MeCN/0.1 mol dm^{-3} TBAB	2.1	0
1h	MeCN/0.1 mol dm^{-3} TBAB	2.1	0

the AB quartet splitting with J=15.3 Hz (cf. for (Z)-**2a**, AB$_q$ J=10.6 Hz[8])). Perusal of the NMR spectra of the reaction mixture indicated that no Z-isomers were produced in any experiment.

Table 2 also shows that there is no significant difference with regard to the product yield and the n-value between MeCN and DMF.

Indirect reduction of **1g** by means of the phenanthrene anion radical showed a catalytic current in the polarogram of phenanthrene in MeCN/TBAP. Nevertheless, the indirect macroelectrolysis of **1g** in MeCN/TBAB at −2.8 V vs. Ag/Ag$^+$ did not give **2g**. The indirect macroelectrolysis of **1i** was not undertaken because no catalytic current was observed.

The coulometric n-values for **1a**—**f** were 3.4—4.2, suggesting that the methylsulfinyl anion resulting from the cleavage of the carbon–sulfur bond will undergo further reduction to produce methanethiol. The production of methanethiol was confirmed experimentally: Benzyl methyl sulfide was isolated though low in yield (22% for **1a**) when the catholyte was allowed to react with benzyl bromide after the electrolysis.

In conclusion, polarography of organic compounds of general formular  $\mathrm{(R)(H)C{=}C(SMe)(S(O)Me)}$ showed that $E_{1/2}$ for the first reduction wave in MeCN or DMF containing excess phenol as a proton donor is slightly dependent on the kind of R in **1** when R is an aryl group, whereas the substrates with R=alkyl are much more difficult to reduce than those with R=aryl. The electrolytic reduction of the substrates with R=aryl involves selective cleavage of one carbon-sulfur bond, resulting in formation of (E)-1-methylthio-2-arylethenes, (E)-**2a**-(E)-**2f**, in good yields with the consumption of about 4 electrons molecule^{-1}. On the other hand, the substrates with R=alkyl did not afford the corresponding desulfinylated compounds although about 2 electrons molecule^{-1} were consumed during the electrolyses. Neither could the corresponding desulfinylated compound be obtained by indirect electrolysis of **1g** by means of phenanthrene anion radical.

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