The Electrolytic Reduction of *p*-Substituted α-(Methylsulfinyl)-α-(methylthio)acetophenones in Acetonitrile

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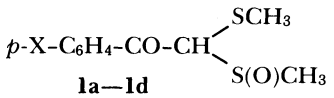
(Received September 28, 1988)

Synopsis. *p*-Substituted α-(methylsulfinyl)-α-(methylthio)-acetophenones (**1**) exhibit, on polarographic reduction, three waves. The two last waves correspond to the reductions of *p*-substituted α-(methylthio)acetophenones (**2**) and *p*-substituted acetophenones respectively. The macroelectrolysis at the first wave potential results in the formation of **2** in good yields in the presence of benzoic acid. The electrolytic reduction of **1** is characterized by the elimination of the methylsulfinyl group rather than by the deoxygenative reduction of the sulfoxide to the sulfide or the reduction of the carbonyl group.

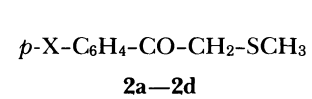
Methylthiomethyl sulfoxide (FAMSO), which is a kind of sulfoxide bearing methylthio group at the α-position, is utilized in a wide variety of organic-synthesis processes. One of the title compounds, α-(methylsulfinyl)-α-(methylthio)acetophenone (**1a**), synthesized with facility from FAMSO and ethyl benzoate, is reduced with sodium tetrahydroborate to afford the corresponding hydroxy compound,[1] while the reaction with copper(II) chloride in 1,2-dimethoxyethane gives PhCOCOSMe.[2]

The present paper is concerned with the electrolytic reduction of the title compounds, *p*-substituted α-(methylsulfinyl)-α-(methylthio)acetophenones (**1**) at mercury, platinum, and lead electrodes in acetonitrile (MeCN). The electrolytic reduction of **1** afforded desulfinylated compounds, *p*-substituted α-(methylthio)acetophenones (**2**), in good yields in the presence of an efficient proton donor. A similar desulfinylation occurs in the electrolytic reduction of 1-methylsulfinyl-1-methylthio-2-arylethenes, which are synthesized from FAMSO and the corresponding aldehydes.[3] Phenacyl phenyl sulfide[4] and sulfoxide[5] also favor the cathodic cleavage of the carbon-sulfur bond, whereas the electrolytic reduction of the carbonyl group predominates for the organosulfur compound bearing the COOH group on the carbon adjacent to the carbonyl group ($HOOCCOCH_2SC_2H_5$).[6] Recently, the electrolytic reduction of diphenyl sulfoxide in nonaqueous media has been reported to afford diphenyl sulfide, together with the benzenesulfinate ion.[7] The above examples show that the cathodic cleavage of the carbon-sulfur bond does not necessarily occur for all the organosulfur compounds.

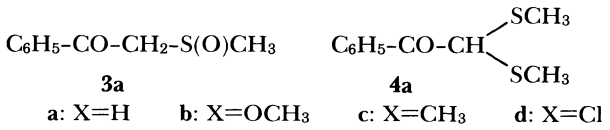
The substrates, **1**, and the related compounds investigated in this work are as follows.



1a—1d



2a—2d



3a **4a**

a: X=H **b**: X=OCH_3 **c**: X=CH_3 **d**: X=Cl

Experimental

The compounds, **1a—1d**, were prepared from FAMSO and ethyl *p*-substituted benzoates according to the published method.[1] The compounds, **1a—1d**, were purified by repeated recrystallizations from a mixture of methanol and water; they showed ^{1}H NMR spectra consistent with the structures assigned.

Polarography and controlled potential macroelectrolysis were carried out, using the experimental set-up and procedure which were reported in a previous paper.[8] All the polarograms were taken in MeCN containing 0.1 (M = mol dm^{-3}) tetrabutylammonium perchlorate (TBAP), the potential being measured against a Ag/0.1 M $AgNO_3$ in MeCN reference electrode (Ag/Ag^+). In the controlled potential macroelectrolysis, tetrabutylammonium tetrafluoroborate (TBAB) were used as the supporting electrolyte, and mercury, platinum, and lead, as the cathode material. After the macroelectrolysis had virtually been completed, the catholyte was carefully concentrated (ca. 3 cm^3), poured into NaCl-saturated water (50 cm^3), and extracted with diethyl ether (3×50 cm^3). After ether-extraction and the usual work-up, the crude mixture and the major product isolated by TLC were subjected to ^{1}H NMR in order to characterize the products.

Results and Discussion

The results of polarography with **1a—1d** are summarized in Table 1. The dc polarogram of **1a** in the absence of proton donors exhibited three waves. In the presence of phenol and benzoic acid, the half-wave potentials ($E_{1/2}$) and wave heights (i_d) of these polarograms were varied, as Table 1 shows. That is, the addition of phenol and benzoic acid caused all the wave heights to increase. On the other hand, the $E_{1/2}$ of the first reduction wave was not changed by adding phenol and benzoic acid, but those of the second and third waves were shifted to more positive potentials. The other substrates, **1b—1d**, exhibited polarographic behavior similar to **1a**. Plots of $E_{1/2}$ vs. the substituent constant sigma gave a good straight line with a slope of 0.50 V for the first reduction wave, indicating that a substrate with a strongly electron-withdrawing group such as Cl is easier to reduce than a substrate with an electron-donating group such as CH_3O.

Controlled potential macroelectrolyses of **1a—1d** at the potential of the first reduction wave were con-

Table 1. Polarographic Half-Wave Potential ($E_{1/2}$) and Wave Height (i_d) of **1a—1d** at a Dropping Mercury Electrode in MeCN Containing 0.1 M TBAP in the Absence and Presence of a Proton Donor

Substrate	Proton donor	$-E_{1/2}$/V vs. Ag/Ag$^+$ [i_d/mA M^{-1}]		
1a	None	1.76 [2.8]	2.29 [0.6]	2.43 [0.2]
	Phenol (4 equiv)	1.76 [5.3]	2.19 [2.4]	2.34 [1.5]
	Benzoic acid (2.2 equiv)	1.76 [10.2]	2.19 [4.5]	2.35 [3.0]
1b	None	1.90 [2.8]	2.38 [0.7]	2.53 [0.3]
	Phenol (4 equiv)	1.90 [5.4]	2.26 [2.3]	2.35 [1.5]
	Benzoic acid (2.2 equiv)	1.90 [10.0]	2.25 [4.7]	2.34 [3.0]
1c	None	1.83 [2.7]	2.32 [0.6]	2.49 [0.2]
	Phenol (4 equiv)	1.83 [5.3]	2.18 [2.5]	2.30 [1.6]
	Benzoic acid (2.2 equiv)	1.83 [10.1]	2.19 [4.9]	2.32 [2.8]
1d	None	1.65 [2.7]	2.12 [0.6]	2.30 [0.2]
	Phenol (4 equiv)	1.65 [5.3]	1.99 [2.5]	2.28 [1.6]
	Benzoic acid (2.2 equiv)	1.65 [10.1]	1.97 [4.3]	2.25 [2.9]

ducted at various cathodes (Hg, Pt, and Pb) in the absence and in the presence of proton donors at room temperature. The substrates, **1a—1d**, were found to undergo the cathodic cleavage of a carbon-sulfur bond to yield *p*-substituted α-(methylthio)acetophenones (**2a—2d**). However, the corresponding hydroxides, *p*-substituted α-(methylsulfinyl)acetophenones (**3**), and *p*-substituted α,α-bis(methylthio)-acetophenones (**4**) were not obtained. Table 2 summarizes the isolated yields of **2a—2d**, along with the coulometric *n*-values (electrons per molecule). The *n*-values were obtained from the amount of the substrate added and the quantity of electricity passed through before the termination of the electrolysis. The yield of **2a** was low in the absence of the proton donor and even in the presence of excess phenol. The addition of benzoic acid caused the yield of **2a** to increase considerably (82%). Therefore, the use of benzoic acid as the proton donor was found to be desirable to improve the yield of **2a**. The kinds of *p*-substituents (X) of the compounds, **1**, and the cathode material (Hg, Pt, and Pb) do not appear to have had a significant influence on the yield of **2**.

Table 3 summarizes the $E_{1/2}$ and i_d values of α-(methylthio)acetophenone (**2a**), α-(methylsulfinyl)acetophenone (**3a**), α,α-bis(methylthio)acetophenone (**4a**), and acetophenone (**5a**) in the presence of proton donors, such as phenol and benzoic acid, together with those of **1a**. If **4a** is an intermediate in the electrolytic reduction of **1a**, the polarographic wave corresponding to the reduction of **4a** must be observed on the polarogram of **1a** because the $E_{1/2}$ value of **4a** is more negative by about 0.17 V than that of **1a**. Such a polarographic wave was not, however, obtained as is shown in Table 3. Furthermore, there was no detectable amount of **4a** in the macroelectrolysis of **1a**. Therefore, it may be concluded that the deoxygenated reduction of the oxygen-sulfur bond in the electrolytic reduction of **1a** does not take place, i.e., the electrolytic redurtion of **1a** does not proceed through **4a**. Similarly, **3a** must also be ruled out as an intermediate in the reductive conversion of **1a** to **2a**, because the polarogram of **1a** did not exhibit the polarographic wave corresponding to the reduction of **3a** and **3a** was not detected in the macroelectrolysis of **1a**. Moreover, Table 3 suggests that the first wave of **1** in the presence of benzoic acid corresponds to a four-electron reduction, since the i_d for the first wave of **1a** was about twice that of **4a** and also, since the i_d for the first wave of **3a**[9] was about twice that of **2a**, when benzoic acid was used as the proton donor.

Tables 2 and 3 indicate that the second and third polarographic waves of **1a** correspond to the reductions of **2a** and **5a** respectively.

On the basis of the above-mentioned results and discussion, it is concluded that the electrolytic reduction of **1** at the potential of the first reduction wave proceeds through neither **3** nor **4**, but through the elimination of the methylsulfinyl group. Also, the reduction of the carbonyl group was found not to occur in the electrolysis of **1**. Furthermore, taking into account the fact that none of the $E_{1/2}$ values of the first reduction wave of **1a—1d** were changed by adding the proton donor, the following scheme may be proposed for the electrolytic reduction of **1** to **2** in the

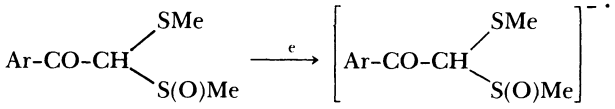
Table 2. Controlled Potential Electrolyses of **1a—1d** at the Potential of the First Reduction Wave in MeCN Containing 0.1 M TBAB

Substrate	Cathode	Potential vs. Ag/Ag$^+$/V	Proton donor (equiv)	*n*-Value	Product (Yield/%)
1a	Hg	−1.80	None	0.8	**2a** (24)
	Hg	−1.80	Phenol (4.0)	2.3	**2a** (58)
	Hg	−1.80	Benzoic acid (2.0)	2.5	**2a** (82)
	Pt	−1.80	Phenol (4.0)	2.2	**2a** (65)
	Pb	−1.70	Phenol (4.0)	2.8	**2a** (50)
1b	Hg	−1.93	Benzoic acid (2.0)	2.9	**2b** (86)
1c	Hg	−1.85	Benzoic acid (2.0)	2.7	**2c** (83)
1d	Hg	−1.68	Benzoic acid (2.0)	2.3	**2d** (80)

Table 3. Polarographic Harf-Wave Potentials ($E_{1/2}$) and Wave Height (i_d) of **1a** and Related Compouds in MeCN Containing 0.1 M TBAP in the Presence of a Proton Donor

Substrate	Proton donor	$-E_{1/2}$ vs. Ag/Ag$^+$/V [i_d/mA M^{-1}]		
1a	Phenol (4.0 equiv)	1.76 [5.3]	2.19 [2.4]	2.34 [1.5]
	Benzoic acid (2.2 equiv)	1.76 [10.2]	2.19 [4.5]	2.35 [3.0]
2a	Phenol (4.0 equiv)		2.18 [4.9]	2.32 [1.6]
	Benzoic acid (2.2 equiv)		2.18 [5.6]	2.33 [1.6]
3a	Phenol (4.0 equiv)	1.89 [5.4]		2.34 [3.3]
	Benzoic acid (2.2 equiv)	1.89 [10.3]		2.35 [3.3]
4a	Phenol (4.0 equiv)	1.93 [4.8]	2.15 [2.9]	2.31 [1.4]
	Benzoic acid (2.2 equiv)	1.93 [5.0]	2.15 [2.9]	2.32 [1.4]
5a	Phenol (4.0 equiv)			2.31 [5.1]
	Benzoic acid (2.2 equiv)			2.32 [5.8]

presence of an efficient proton donor:



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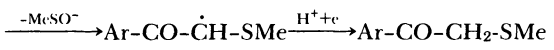

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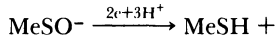

It is not clear whether or not the methylsulfinyl anion resulting from the cleavage of the carbon-sulfur bond undergoes further reduction to yield methanethiol, since the formation of methanethiol has not yet been ascertained and since the above mechanism indicates that **1** is reduced in an overall four-electron process (the coulometric n-values obtained were 2.2—2.9 for **1a—1d**, even in the presence of the proton donor). However, the polarographic n-value for the first reduction wave of **1** was 4, suggesting that the reduction of methylsulfinyl anion to methanethiol occurs at the reduction potential of **1**. Furthermore, it has been reported that the electrolytic reduction of 1-methyl-sulfinyl-1-methylthio-2-phenylethene afforded desulfinylated compounds, 1-methylthio-2-phenylethene and methanethiol, with the consumption of 3.6 electrons per molecule.[3] Accordingly, from the evidence that the coulometric n-values were more than 2 in the presence of the proton donor, as is shown in Table 2, together with above considerations, it seems reasonable to conclude that a part of the methylsulfinyl anions are electrochemically reduced to afford methanethiol. The remainder will be converted chemically to methanethiol etc., since methane sulfenic acid, if formed at all, is very unstable.

References

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9) The macroelectrolysis of **3a** gave **5a** in a 70% yield.