The Cathodic Desulfonylation of 1-Ethoxycarbonyl- and 1-Cyano-1-(*p*-tolylsulfonyl)-2-phenylethenes at the Mercury Electrode in Nonaqueous Solvents

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Synopsis. The cathodic reduction of 1-ethoxycarbonyl-1-(*p*-tolylsulfonyl)-2-phenylethene in MeCN and DMF is characterized by the selective elimination of the *p*-tolylsulfonyl group, resulting in the formation of ethyl (*E*)-cinnamate in good yields, in the presence of such efficient proton donors as benzoic acid and acetic acid. On the other hand, the cathodic desulfonylation of 1-cyano-1-(*p*-tolylsulfonyl)-2-phenylethene proceeds with low efficiencies, even in the presence of acetic acid and benzoic acid.

The cathodic desulfurization of organosulfur compounds has received considerable attention because most of them are valuable synthetic precursors. In general, α,β-unsaturated sulfides, sulfoxides, and sulfones are much more subject to cathodic desulfurization than to the hydrogenation of the double bond.[1-6] For example, the previous paper[6] showed that the cathodic reduction of 1-methylthio-1-(*p*-tolylsulfonyl)-2-arylethenes in nonaqueous solvents involves the selective cleavage of a carbon–sulfur bond, resulting in the formation of (*E*)-1-methylthio-2-arylethenes in moderate yields with the consumption of about 2 electrons per molecule, in the presence of such efficient proton donors as phenol and benzoic acid. The cathodic reduction of vinyl sulfones with the electron-withdrawing group at Position 1, such as the title compounds, 1-ethoxycarbonyl-1-(*p*-tolylsulfonyl)-2-phenylethene (**1**) and 1-cyano-1-(*p*-tolylsulfonyl)-2-phenylethene (**2**), is also of interest in connection with the reductive desulfonylation. Moreover, they may be expected to afford the corresponding desulfonylated compounds in a manner similar to the cathodic reduction of 1-methylthio-1-(*p*-tolylsulfonyl)-2-phenylethene.[6]

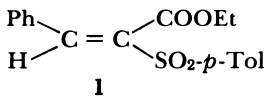
In the present work, the electrolytic reductions of **1** and **2** at a mercury electrode in nonaqueous media, such as acetonitrile (MeCN) and *N*,*N*-dimethylformamide (DMF), were studied by means of polarography, coulometry, and controlled-potential macroelectrolysis. The substrates, **1** and **2**, gave the corresponding desulfonylated compounds, (*E*)-ethyl cinnamate (**3**) and (*E*)-cinnamonitrile (**4**) respectively, but their yields were greatly dependent on the kind of electrolytic solution.

Experimental

The title compound, **1**, was synthesized by a condensation of benzaldehyde with ethyl (*p*-tolylsulfonyl)acetate according to a method described in the literature.[7] Ethyl (*p*-tolylsulfonyl)acetate was prepared starting from ethyl bromoacetate and sodium *p*-toluenesulfinate according to the published method:[8]

$$BrCH_2COOEt + p\text{-}TolSO_2Na \xrightarrow[\text{in DMF}]{} EtOOCCH_2SO_2\text{-}p\text{-}Tol$$

$$EtOOCCH_2SO_2\text{-}p\text{-}Tol + PhCHO \xrightarrow[\text{in benzene}]{\text{Piperidine}}$$



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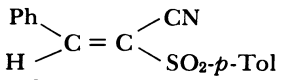
Similarly, **2** was synthesized from benzaldehyde and (*p*-tolylsulfonyl)acetonitrile,[7] which had itself been prepared starting from chloroacetonitrile and sodium *p*-toluenesulfinate according to the published method:[8]

$$ClCH_2CN + p\text{-}TolSO_2Na \xrightarrow[\text{in EtOH}]{} NCCH_2SO_2\text{-}p\text{-}Tol$$

$$NCCH_2SO_2\text{-}p\text{-}Tol + PhCHO \xrightarrow[\text{in DMF}]{\text{Triton B}}$$



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The substrates, **1** and **2**, were purified by recrystallization from a benzene–hexane mixture and from ethanol respectively; they were identified by means of their ^{1}H NMR spectra.

The nonaqueous acetonitrile solutions were prepared from predeoxygenated MeCN and tetrabutylammonium tetrafluoroborate (TBAB) or tetrabutylammonium perchlorate (TBAP), which had been purified and dried as has been described previously.[4] The nonaqueous *N*,*N*-dimethylformamide solutions were similarly prepared from the predeoxygenated DMF and TBAB or TBAP. DMF was purified in a manner similar to that described in the literature.[9] The concentration of the supporting electrolyte was 0.1 mol dm^{-3}. The phenol, acetic acid, and benzoic acid used as proton donors were purified by means of distillation or sublimation.

A Ag/0.1 mol dm^{-3} $AgNO_3$ in MeCN reference electrode (Ag/Ag^+) and a Ag/AgI, 0.1 mol dm^{-3} TBAI in DMF reference electrode (Ag/AgI) were used respectively, depending on the kind of solvent used. Polarography, coulometry, and controlled potential macroelectrolysis were carried out, using the same experimental set-up and procedure as were reported in the previous paper.[6]

Results and Discussion

Polarography. The influence of the proton donor on the dc polarograms of **1** and **2** at a dropping mercury electrode was examined in MeCN/TBAP and DMF/TBAP. Phenol, acetic acid, and benzoic acid were used as the proton donors. Among the media studied, the strongest influence on the polarogram was observed in the medium of MeCN/benzoic acid. Table 1 summarizes the half-wave potential ($E_{1/2}$) and the wave height (i_d) of the first reduction wave in various electrolytic solutions. As may be seen from Table 1, there is some difference among the proton donors used with respect to the influence of the proton donor on $E_{1/2}$ and i_d. That is, the $E_{1/2}$ of the first wave of **1** in MeCN was shifted to more positive values by the addition of acetic acid or benzoic acid, but $E_{1/2}$ in DMF was not changed. On the other hand, the $E_{1/2}$ of **2** was not influenced, not even in the medium of MeCN/benzoic acid. The influence of the proton donor on i_d was also observed; these results are also presented in Table 1.

Macroelectrolysis. A series of controlled potential macroelectrolyses of **1** and **2** at each plateau potential of the first reduction wave were carried out at the stirred mercury pool electrode in MeCN/TBAB and DMF/TBAB in the absence and in the presence of proton donors at room temperature. The results are summarized in Table 2. The coulometric n-values (electrons per molecule) were obtained from the amount of the substrate added and the quantity of electricity passed through before the termination of the electrolysis. Table 2 shows that the substrate with the COOEt group, **1**, affords the desulfonylated compound, **3**, and methyl p-tolyl sulfone (**5**) in good yields, in MeCN and DMF containing excess acetic acid and benzoic acid, whereas the yields of **3** and **5** were low in the absence of the proton donor and even

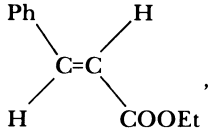
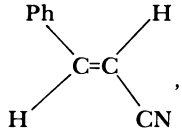
Table 1. Polarographic Data of the First Reduction Wave of **1** and **2** in MeCN and DMF Containing 0.1 mol dm^{-3} in the Absence and Presence of Proton Donors

Substrate	Solvent	Proton donor (equiv)	$-E_{1/2}$/V[a]	I_d/mA mol^{-1}
1	MeCN	None	1.71	3.2
		Phenol (4.0)	1.71	3.5
		Acetic acid (4.0)	1.66	6.5
		Benzoic acid (4.0)	1.64	7.2
	DMF	None	1.00	2.3
		Phenol (4.0)	1.00	2.3
		Acetic acid (4.0)	1.00	2.9
		Benzoic acid (4.0)	1.00	4.2
2	MeCN	None	1.46	3.7
		Phenol (4.0)	1.46	3.7
		Acetic acid (4.0)	1.46	3.7
		Benzoic acid (4.0)	1.46	4.5
	DMF	None	0.78	2.6
		Phenol (4.0)	0.78	2.6
		Acetic acid (4.0)	0.78	2.6
		Benzoic acid (4.0)	0.78	2.6

a) Against Ag/Ag$^+$ in MeCN and Ag/AgI in DMF.

Table 2. Controlled Potential Electrolysis of **1** and **2** at the First Reduction Potential on the Hg Pool Cathode in Nonaqueous Media Containing 0.1 mol dm^{-3} TBAB

Substrate	Solvent	Proton donor (equiv)	n-Value	Product[a]	(Yield/%)
1	MeCN	None	0.8	**3** (Trace)	**5** (Trace)
		Phenol (4.0)	1.3	**3** (30)	**5** (30)
		Acetic acid (4.0)	1.6	**3** (75)	**5** (69)
		Benzoic acid (4.0)	1.7	**3** (72)	**5** (62)
	DMF	None	0.7	**3** (Trace)	**5** (Trace)
		Phenol (4.0)	1.0	**3** (7)	**5** (Trace)
		Acetic acid (4.0)	1.5	**3** (74)	**5** (66)
		Benzoic acid (4.0)	1.6	**3** (70)	**5** (61)
2	MeCN	Phenol (4.0)	1.0	**4** (7)	**5** (Trace)
		Acetic acid (4.0)	1.2	**4** (13)	**5** (15)
		Benzoic acid (4.0)	1.5	**4** (29)	**5** (22)
	DMF	Phenol (4.0)	0.9	**4** (Trace)	**5** (Trace)
		Acetic acid (4.0)	1.0	**4** (4)	**5** (Trace)
		Benzoic acid (4.0)	1.1	**4** (8)	**5** (Trace)

a) **3**:  , **4**:  , **5**: p-TolSO$_2$Me.

in the presence of excess phenol. **5** was obtained as a product by a CH_3I methylation of the *p*-toluenesulfonyl anion formed upon electrolysis. It is worth noting that phenol is an effective proton donor in the cathodic desulfonylation of 1-methylsulfonyl-1-methylthio-2-phenylethene in both MeCN and DMF, but not in the case of **1**.

On the other hand, the electrolytic reduction of **2** afforded the desulfonylated compounds, **4** and **5**, in low yields, even in the presence of acetic acid. The yields of **4** and **5**, although still low, were increased to 29 and 22% respectively in the medium of MeCN/benzoic acid. Even though **2** was easier to reduce than **1**, the cathodic desulfonylation proceeded with a low efficiency compared with **1**. This seems to be not because the desulfonylated compound is subject to further reduction, but because the polymerization of a reduction intermediate of **2** proceeds in preference to the desulfonylation, although the polymeric products could not be characterized. This is supported by the evidence that coulometric *n*-values are low and that **4** is not easier to reduce than **2**. The stereochemical structures of **3** and **4** was determined on the basis of the NMR spectra of their olefinic protons. A perusal of the NMR spectra of the reaction mixtures indicated no formation of (*Z*)-isomers of **3** and **4** in any experiment.

The combination of Tables 1 and 2 indicates that the proton donor causing an increase in i_d by its addition has a tendency to bring about the cathodic desulfonylation with a high efficiency.

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