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Studies on Sulfenamides. VIII.¹⁾ Anodic Oxidation of 2-Nitrobenzene-sulfenamides Derived from Secondary Cyclic Amines

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Methyl 2-nitrobenzenesulfenate (**5**) was formed by controlled potential electrolysis (CPE) of *N*-(2-nitrophenylthio)amines (morpholine (**1**), piperidine (**2**), pyrrolidine (**3**), thiomorpholine (tetrahydro-4*H*-1,4-thiazine) (**4**)) in methanol at a glassy carbon anode. A yellow powder obtained by the electrolysis of **1** reacted with triethylamine to give 2,4-bis(*o*-nitrophenylthio)-5,6-dihydro-1,4-oxazine (**7**). CPE of **1**—**4** in acetonitrile gave 2,2'-dinitrodiphenyldisulfide (**6**).

These results suggest that the initial step of anodic oxidation of **1**—**4** in acetonitrile is an EC process (an electron transfer process followed by a chemical reaction), while that in methanol is an ECE process (an electron transfer process followed by a chemical reaction and then an electron transfer process). Enamine is considered to be one of the intermediates in the anodic oxidation of **1**—**4** in methanol.

Keywords—anodic oxidation; 2-nitrobenzenesulfenamide; enamine; sulfenate; dihydro-oxazine

In the previous papers,^{1,2)} we reported the anodic and chemical oxidation of benzene-sulfenanilides and 2-nitrobenzenesulfenanilides in detail. In order to elucidate the mechanism of oxidation of sulfenamides more clearly, controlled potential electrolysis (CPE) of *N*-(*o*-nitrophenylthio)amines (morpholine (**1**), piperidine (**2**), pyrrolidine (**3**), thiomorpholine (**4**)) in methanol and in acetonitrile containing 0.1 M NaClO₄ at a glassy carbon anode was investigated.

Results and Discussion

Table I summarizes the results of CPE of **1**—**4** in methanol and in acetonitrile.

TABLE I. Results of Controlled Potential Electrolysis^{a)} of
N-(*o*-Nitrophenylthio)amines (10 mM) in Methanol
and Acetonitrile Containing 0.1 M NaClO₄
at a Glassy Carbon Anode

Compd. No.	In MeOH		In MeCN	
	<i>n</i> -Value	Yield of 5 , mol%	<i>n</i> -Value	Yield of 6 , mol%
1	1.8	21.0 ^{b)}	0.76	10.8
2	2.7	23.0	0.82	Trace
3	2.0	36.6	0.92	Trace
4	1.7	56.0	0.67	13.6

a) 1.2 V vs. S.C.E.

b) 2,4-Bis(*o*-nitrophenylthio)-5,6-dihydro-2*H*-1,4-oxazinium perchlorate (74.2%) is also formed.

chloride and enamine could give a product similar to **6**.³⁾

In the case of oxidation of sulfenamidides, the nitrenium ion could be trapped as phenazines,^{2a,b)} but in the case of **1**—**4**, no product from C and F were identified. Thus, the fate of C and F is unknown at present.

Electrolysis of **2**—**4** can be considered to be analogous with that of **1**.

Experimental

Materials—Sulfenamides were prepared from 2-nitrobenzenesulfonyl chloride and the corresponding amines by the method of Capron,⁴⁾ and purified by crystallization from 90% ethanol except in the case of **2**, which is a liquid at room temperature and was purified by column chromatography on alumina. Each compound gave analysis results consistent with the theoretical values.

Methanol was dried with activated magnesium and distilled.

Apparatus—Controlled potential electrolysis was carried out as described previously.²⁾ HPLC was carried out with Waters Associates M-45 solvent delivery system, U6K universal LC injector, Z-module radial compression separation system, and Uvidec-100 (Japan Spectroscopic Co.). IR, nuclear magnetic resonance (NMR), and mass spectra (MS) were obtained as described previously.²⁾

Isolation of **5**: **4** (259.9 mg) was subjected to electrolysis in methanol (100 ml) containing 0.1 M NaClO₄ at 1.2 V (vs. S.C.E.) at room temperature. The electrolyzed solution was concentrated under reduced pressure to one-third of its original volume. The concentrated solution was added to 10% HCl (100 ml) and the mixture was extracted with ether. The organic layer was washed with water, dried with Na₂SO₄, and evaporated to give a red oil. The oil was subjected to column chromatography on alumina with benzene as the eluent. The yellow effluent was evaporated to dryness under reduced pressure. The residue (86.6 mg) was identified as **5**⁵⁾ on the basis of IR spectra.

Isolation of **7**: **1** (240.0 mg) was subjected to electrolysis in methanol (100 ml) containing 1.2 g of NaClO₄ at 1.2 V at room temperature until the current fell below 1% of the initial value. The quantity of electricity consumed (170.3 C) corresponded to $n = 1.8$. A yellow powder separated out, and was filtered off and weighed (176.6 mg).

Triethylamine (0.25 ml) was added to a mixture of CH₃CN (10 ml) and the yellow powder (655.3 mg). The mixture was stirred overnight, then added to ether (100 ml), and the whole was stirred for an hour before filtration. The filtrate was evaporated to dryness under reduced pressure, and the residue was subjected to column chromatography on alumina with benzene as the eluent. The yellow effluent was evaporated to dryness under reduced pressure, and the residue was recrystallized from acetone, and weighed (114.1 mg). It was identified as **7** on the basis of the elemental analysis data, and IR, NMR, and MS. *Anal.* Calcd for C₁₆H₁₅N₃O₅S₂: C, 49.10; H, 3.35; N, 10.74. Found; C, 47.86; H, 4.03; N, 9.76. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1320 (NO₂), 1055 (=C—O—C). NMR (CDCl₃) δ : 3.7—4.2 (2H, m, methylene proton), 4.4—4.8 (2H, m, methylene proton), 5.7 (H, s, vinyl proton), 7.3—8.6 (8H, m, aromatic proton). MS m/e : 237 (M⁺—O₂N—C₆H₄—S⁺), 391 (M⁺).

Determination of **5**: Ten μ l of the solution from electrolysis was subjected to HPLC using radial-pak μ Bondapak C₁₈ with CH₃OH—H₂O (1 : 1) as the eluent. The detector was operated at 254 nm.

Determination of **6**: **6** was determined by the same procedure as **5**, but with CH₃OH—H₂O (2 : 1) as the eluent.

References

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