Notes

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Studies on Sulfenamides. VIII.[1] Anodic Oxidation of 2-Nitrobenzenesulfenamides 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; dihydrooxazine

In the previous papers,[1,2] we reported the anodic and chemical oxidation of benzenesulfenanilides 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 $NaClO_4$ 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 $NaClO_4$ at a Glassy Carbon Anode

Compd. No.	In MeOH		In MeCN	
	n-Value	Yield of **5**, mol%	*n*-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.

The yields of methyl 2-nitrobenzenesulfenate (**5**) and 2,2′-dinitrodiphenyldisulfide (**6**) were determined by high performance liquid chromatography (HPLC).

A yellow powder precipitated from the electrolyzed solution in the last stage of CPE of **1** in methanol. This compound was explosive, and its infrared (IR) spectrum showed a characteristic absorption band of the Cl–O bond at 1105 cm^{-1}. They reacted with triethylamine in acetonitrile to give 2,4-bis(*o*-nitrophenylthio)-5,6-dihydro-1,4-oxazine (**7**) as shown in Chart 1. Thus, the yellow powder was presumed to be 2,4-bis(*o*-nitrophenylthio)-5,6-dihydro-2*H*-1,4-oxazinium perchlorate (**8**).

The following schemes are suggested for the anodic oxidation of **1**.

Anodic oxidation of **1** gives the cation radical (A). In acetonitrile, which is an aprotic solvent, A undergoes homolytic cleavage of the S–N bond, and gives **6**. Schemes 1—3 are supported by the coulometric *n*-value of 0.76.

In methanol, which is a protic solvent, A undergoes deprotonation followed by an electron transfer process, and gives cation D. A coulometric *n*-value of 1.8 supports schemes 1 and 4. A part of D undergoes cleavage of the S–N bond and gives the sulfenylium ion (E), and a part of E reacts with methanol to give **5**. The rest of D undergoes cleavage of the β-C–H bond and gives the enamine G. A product of reaction of G with E is precipitated as the yellow powder, namely **8**. Kuehne has shown that electrophilic substitution of 2-nitrobenzenesulfenyl

Ar : 2-nitrophenyl
Et : ethyl

Chart 1

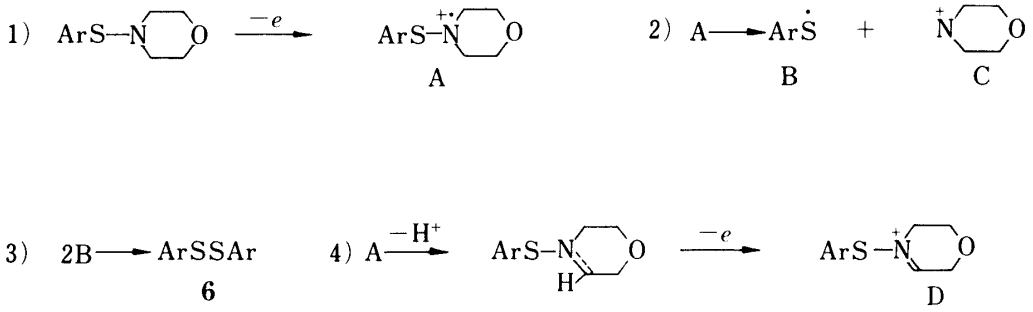

Chart 2

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

In the case of oxidation of sulfenanilides, 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-nitrobenzenesulfenyl 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 $NaClO_4$ 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 Na_2SO_4, 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 $NaClO_4$ 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 CH_3CN (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 $C_{16}H_{15}N_3O_5S_2$: C, 49.10; H, 3.35; N, 10.74. Found; C, 47.86; H, 4.03; N, 9.76. IR ν_{max}^{KBr} cm^{-1}: 1320 (NO_2), 1055 (=C–O–C). NMR ($CDCl_3$) 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 ($M^+ - O_2N - C_6H_4 - S^+$), 391 ($M^+$).

Determination of **5**: Ten μl of the solution from electrolysis was subjected to HPLC using radial-pak μBondapack C_{18} with CH_3OH–H_2O (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 CH_3OH–H_2O (2 : 1) as the eluent.

References

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