was added dropwise by syringe to a slight excess (12 mL, 97.4 mmol) of trimethylacetyl chloride in 50 mL of the THF while maintaining a positive N_2 pressure. The reaction mixture was stirred 0.5 h after addition was complete and then 15 mL of water was added. The THF was removed in vaccuo and the product was extracted with a 3 × 75 mL portion of hexane. The hexane extract was washed with dilute HCl and dried over $MgSO_4$.

Concentration of the hexane and distillation gave 2-(3-oxo-4,4-dimethylpentyl)-1,3-dioxane (12.34 g, 61.7 mmol): bp 115–122 °C (7 mm); IR (neat) 2962, 2851, 1708, and 1149 cm^{-1}; NMR (CCl_4) δ 1.11 (s, 9 H), 1.2–2.2 (m, 4 H), 2.3–2.7 (m, 2 H), 3.4–4.3 (m, 4 H), and 4.45 (t, 1 H).

This compound was hydrolyzed to 8 as follows. In a 50-mL flask equipped with magnetic stirring was placed 40 mL of H_2O and 5.34 g of 2-(3-oxo-4,4-dimethylpentyl)-1,3-dioxane and 1 g of oxalic acid. A Dean-Stark trap modified to return the bottom layer was attached and filled with water. The mixture was refluxed for 3 h, steam distilling 8 into the trap. The product was taken up in 10 mL of ether, dried over $MgSO_4$, concentrated, and distilled in vacuo (bp 88 °C (12 mm)). The yield was 2.30 g (6.12 mmol, 61%): IR (neat) 2968, 2825 (shoulder), 2718, 1725, and 1707 cm^{-1}; NMR (CCl_4) δ 1.14 (s, 9 H), 2.50 (s, 4 H), and 9.80 (s, 1 H).

Synthesis of the Trimer of 3-*tert*-Butyl-4,5-dihydropyridazine (10). In a 100-mL flask equipped with N_2 atmosphere, condenser, and magnetic stirring was placed 50 mL of benzene and 3.01 g (21.2 mmol) of 4-oxo-5,5-dimethylhexanal. Hydrazine (97%, 2 mL, 63 mmol) was added dropwise. After stirring at reflux for 1 h a Dean-Stark trap was attached and the water azeotroped off over a 2-h period. The benzene was removed in vaccuo and the oil produced was crystallized by addition of 95% ethanol. A second crop of crystals was obtained by addition of water to the ethanol. The yield was 1.30 g (9.4 mmol, 44%): mp 123–125 °C; IR ($CHCl_3$) 2960, 1624, 1475, and 1362 cm^{-1}; NMR δ 1.09 (s, 9 H), 1.9–2.6 (m, 4 H), and 3.2–3.6 (m, 1 H). Mass spectrum showed a large parent ion at 414 ± 1.

Anal. Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.36; H, 10.34; N, 20.14.

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Registry No.—**2**, 37819-05-9; **7**, 36046-77-2; **7** *N*-acetyl derivative, 36046-34-1; **8**, 66662-24-6; **10**, 66842-46-4; 2,5-dimethoxytetrahydrofuran, 696-59-3; hydrazine, 302-01-2; 2-(2-bromoethyl)-13-dioxane, 33884-43-4; trimethylacetyl chloride, 3282-30-2; 2-(3-oxo-4,4-dimethylpentyl)-1,3-dioxane, 66842-47-5; 4,5-dihydropyridazine, 56962-82-4.

Supplementary Material Available: Table I listing final refined coordinates and anisotropic temperature factors (isotropic for hydrogen atoms) (3 pages). Ordering information is given on any current masthead page.

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Kinetics of the Rearrangement of *N*-Nitroso(2-methylamino)acetonitrile in Basic Methanol by Differential Pulse Polarography

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Daeniker[2] had reported earlier that *N*-nitroso(2-methylamino)acetonitrile (I) undergoes an interesting rearrangement in basic methanol solution to yield α-isonitroso-*N*-methylaminoacetonitrile (II) (eq 1). During the course of electroanalytical studies on I and other *N*-nitrosamines we observed that the kinetics of this reaction could be studied by differential pulse polarography. A similar application of this technique had been used by us to study the anchimeric role of the nitroso group in the aqueous basic hydrolysis of I.[3] The current study lends support to the mechanism of rearrangement proposed by Daeniker and, in addition, outlines an isolation procedure for II that gives considerably improved yields.

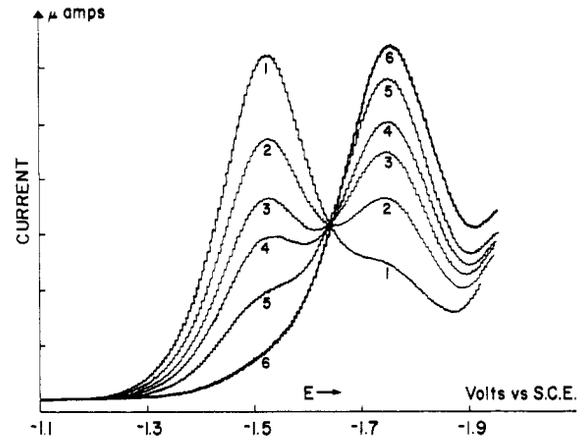


Figure 1. Differential pulse polarograms of rearrangement of *N*-nitroso-2(methylamino)acetonitrile in basic methanol solution: Supporting electrolyte 0.1 M Et_4NClO_4; temperature 22 °C; [OH^-] = 0.006 M; scan rate 5 mV/s; drop time 1.0 s; pulse amplitude 50 mV (p-p); Hg flow rate 1.20 mg/s. Curve 1: 0 min. Curve 2: 6 min. Curve 3: ~12 min. Curve 4: ~20 min. Curve 5: ~32 min. Curve 6: ~105 min.

$$\underset{\underset{N{=}O}{|}}{CH_3NCH_2CN} \xrightarrow[\text{Base}]{\text{ROH}} \underset{\underset{NOH}{\|}}{CH_3NHCCN} \qquad (1)$$

I II

In neutral methanol, I displays a single, diffusion-controlled, differential pulse polarographic peak at −1.52 V vs. SCE. In the presence of methoxide ion, however, the expected peak is followed by a second peak (−1.74 V), an unusual result for a nitrosamine.[4] The heights of the two peaks vary in a regular fashion as a function of time. Typical results are shown in Figure 1; curves 1–6 were recorded on the same solution over a period of approximately 100 min. The species giving rise to the second peak is stable; once it is fully formed the peak height remains constant over a period of 12 h.

The most logical explanation for the observed polarographic results is that proposed by Daeniker (Scheme I). To insure that the reaction described by eq 1 is occurring in the polarographic cell and that II is the species giving rise to the second peak, the solution conditions used in the polarographic cell were repeated on a preparative scale. The physical and spectral data for the sublimed product isolated were identical

Scheme I

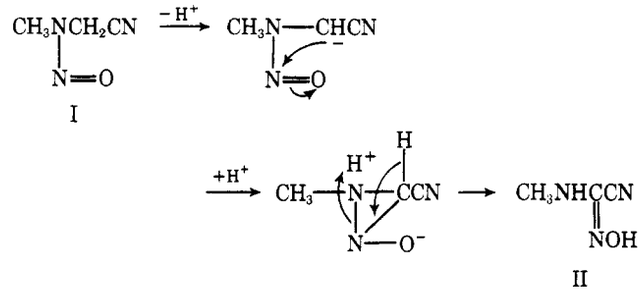


Table I. Kinetic Data for the Rearrangement of *N*-Nitroso(2-methylamino)acetonitrile in Basic Methanol

t, °C	k, L mol^{-1} s^{-1}
1.0 ± 0.02	(5.96 ± 0.07) × 10^{-3}
11.0 ± 0.02	(1.41 ± 0.19) × 10^{-2}
23.0 ± 0.02	(3.32 ± 0.09) × 10^{-2}

$\Delta H^{\ddagger}$ = 12.0 ± 0.34 kcal mol^{-1} $\Delta S^{\ddagger}$ = −24.7 eu

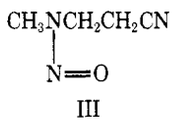
with those of α-isonitroso-*N*-methylaminoacetonitrile reported earlier.[2] A polarogram obtained after addition of the isolated crystals to the solution that yielded curve 6 (Figure 1) showed an increase in peak height without any shift in peak potential, strongly suggesting that the isolated product is the species giving rise to the peak at −1.74 V.

The kinetics of the reaction in eq 1 were determined by measuring the rate of decay of the peak current at −1.52 V, i.e., at the peak potential of species I. Kinetic studies were performed at 1.0, 11.0, and 23 °C.

The reaction was found to be second order (first order with respect to both I and base). The second-order rate constants and activation parameters were calculated in the usual fashion[6] and are given in Table I. The most significant value in the table is the large negative entropy of activation. A pathway that agrees with the kinetic observations is shown in Scheme I; a similar mechanism involving a three-membered ring was first suggested by Daeniker.[2]

The transformation of I to II is facilitated by the relatively high acidity of the methylene protons. The anion that forms is stabilized by the adjacent *N*-nitroso and nitrile groups. To check this conclusion, the next higher homologue of I, *N*-nitroso(3-methylamino)propionitrile (III), was examined polarographically under identical experimental conditions. Compound III gave single differential pulse polarographic peaks in *both* neutral and basic methanol solutions that remained unchanged over a period of 12 h.

The strong acidity of the methylene protons in I is further supported by NMR studies. At room temperature in D_2O, I incorporates two deuteriums instantaneously to yield I-D_2. No such incorporation occurs with III.



III

Experimental Section

α-Isonitroso-*N*-methylaminoacetonitrile (II) from *N*-Nitroso(2-methylamino)acetonitrile (I). Dry methanol (20 mL) was placed in a round-bottom flask fitted with a drying tube and a side arm for the passage of N_2 gas. Dry N_2 was bubbled through the solution for 10 min. A freshly cut piece of sodium metal (0.2 g) was then added and, after it had reacted, I (1.0 g) was added. The solution was allowed to remain at room temperature for 5 h in a nitrogen atmosphere and then evaporated to dryness under vacuum. The residue was dissolved in water (30.0 mL) and adjusted to pH 6.5 with hydrochloric acid. The solution was evaporated to dryness under vacuum and the residue was extracted with chloroform (300 mL). The chloroform solution was evaporated to dryness under vacuum and the residue was sublimed under vacuum yielding white needle-shaped crystals (0.5 g, 50%; mp 154–156 °C (lit.[2] mp 155–157 °C)): single spot on TLC; NMR (D_2O), $-CH_3$, δ 2.90 (s, 3 H); IR 2.93 (OH), 3.12 (NH), 4.42 (C≡N), 6.01 μm (C=N); UV_{max} in absolute ethanol 2550 Å. Anal. Calcd: C, 36.36; H, 5.05. Found: C, 36.39; H, 5.10.

Kinetics of I → II.[6] Methanol solutions of constant ionic strength containing tetrapentylammonium iodide as supporting electrolyte and base were prepared. A 10^{-2} M solution of I in methanol was used as stock solution. The cell was thermostated at 1, 11, and 23 °C using Forma Scientific Model 2095 refrigerated and heated bath and circulator. The decrease in peak current was monitored by recording successive polarograms at fixed time intervals. All the observations were made twice to check the reproducibility of the results. In all cases a plot of ln I_p vs. t was linear and independent of concentration of I, indicating the transformation to be first order with respect to I. The pseudo-first-order rate constants were calculated from the slope of ln I_p vs. t. Variation of the pseudo-first-order rate constants with concentration of base was linear at all temperatures, yielding a first-order reaction rate with respect to base. Second-order rate constants were calculated and are given in Table I. The activation parameters were calculated in the usual fashion.[6]

Spectra and Differential Pulse Polarography. NMR, UV, and IR spectra and differential pulse polarograms were obtained as previously described.[3]

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Registry No.—I, 3684-97-7; II, 66922-13-2; III, 60153-49-3.

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Stopped-Flow Study of Salt Effects on the Hydroxide and Borate Ion Catalyzed Hydrolysis of Covalent *p*-Tolylsulfonylmethyl Perchlorate in Aqueous Borax Buffer Solutions

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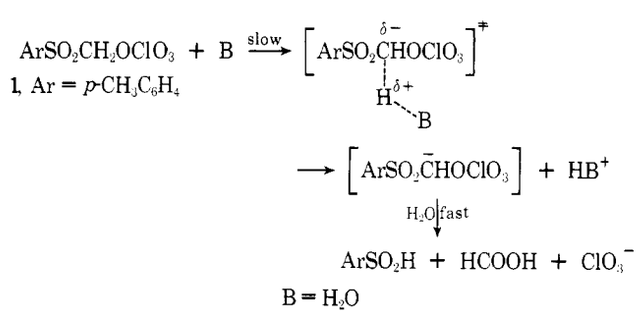
As part of a detailed study of environmental[1,2] and micellar effects[3] on the general base-catalyzed hydrolysis of covalent[4] arylsulfonylmethyl perchlorates, we have recently reported kinetic salt effects on the water-catalyzed process.[2] This pH-independent hydrolysis involves rate-determining proton transfer from the reactant to water via a dipolar transition state in which the negative charge at the α-sulfonyl carbon atom is highly dispersed.[1,5] The electrolyte effects were rationalized mainly by invoking the importance of electrostatic ion–water interactions in the joint cybotactic regions of the ions and the reactant and/or transition state. This theory



emerged as a result of the observation that the salt effects were predominantly governed by the charge type and density of the distinct ions.[2] Electrolyte-induced changes in water structure were assigned a secondary role. As an extension of these studies, we now report the effects of some neutral electrolytes on the rates of hydroxide and borate ion catalyzed hydrolysis in aqueous borax buffer solutions of constant ionic strength (I = 1.0 M). The main objective of this work was to see

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