disodium salt of 4-cyano-3,5-(dimercapto)isothiazole (**5**) gave 4-cyano-3,5-bis[(chloromethyl)thio]isothiazole (**6**) in 60% yield (eq 7).

## Experimental Section[6]

**1-[(Chloromethyl)thio]-4-(1,1-dimethylethyl)benzene.** To a slurry of 6.50 g (0.10 mol) of finely powdered 85% potassium hydroxide in 300 mL of bromochloromethane were added 12.5 g (0.10 mol) of 4-(1,1-dimethylethyl)benzenethiol. To this mixture, 0.125 g (0.00055 mol) of benzyltriethylammonium bromide was added, and the reaction mixture was stirred at 25–30 °C for 0.5 h. The reaction mixture was amber in color, and a pale yellow solid had precipitated. The reaction mixture was filtered, and the bromochloromethane removed in vacuo leaving a light amber oil. The oil was dissolved in 100 mL of ether, and the resulting solution filtered through anhydrous magnesium sulfate. The ether was removed in vacuo from the filtrate leaving 16.5 g of nearly colorless oil. The oil was distilled under reduced pressure to give 12.30 g (60% yield) of the title compound as a colorless liquid, bp 100–106 °C (3 mm).

**1-[(Chloromethyl)thio]-2,4,6-tribromobenzene.** To a slurry of 1.63 g (0.025 mol) of finely powdered 85% potassium hydroxide in 150 mL of bromochloromethane was added 8.70 g (0.025 mol) of 2,4,6-tribromobenzenethiol. To this mixture, 0.30 g of benzyltriethylammonium bromide was added, and the temperature rose from 26 to 28 °C in several minutes. The reaction mixture was stirred for 2 h and then filtered to remove the sodium bromide which separated. The bromochloromethane was removed in vacuo from the filtrate leaving a light, red-brown oil. The oil was treated with 75 mL of ether dissolving most of the material and leaving a small amount of red-brown oil. The ether solution was dried over anhydrous magnesium sulfate and filtered. The ether was diluted with an equivalent amount of hexane, and the resulting solution concentrated in vacuo to give 4.20 g of the title compound, mp 71–72 °C. Further concentration gave an additional 4.80 g, mp 71–72 °C (total yield 91%).

**2-[(Chloromethyl)thio]-6-ethoxybenzothiazole.** To a well-stirred slurry of 105.7 g (0.50 mol) of 6-ethoxy-2-mercaptobenzothiazole in 1 L of bromochloromethane were added 32.5 g (0.50 mol) of finely powdered 85% potassium hydroxide and 1.0 g of benzyltriethylammonium bromide. The temperature of the reaction mixture slowly rose from 23 to 38 °C over a period of 1.75 h. The stirring was continued for an additional 1 h, during which the temperature slowly fell to 32 °C. The precipitated potassium bromide was filtered off, and the organic filtrate washed with 500 mL of water. The organic layer was dried over anhydrous calcium chloride, and the bromochloromethane removed in vacuo leaving a damp powder. The powder was slurried with anhydrous diethyl ether to give an insoluble white powder which was filtered and dried to give 102 g of the title compound, mp 112–113 °C. A 24-g second crop was obtained from the ether filtrate (total yield 93%). A sample of this material was recrystallized from chloroform to give white plates, mp 112–113 °C.

**2,5-Bis[(chloromethyl)thio]-1,3,4-thiadiazole (4).** A slurry of 100 g (0.44 mol) of the dipotassium salt of 2,5-dimercapto-1,3,4-thiadiazole (**3**) in 850 mL of bromochloromethane containing 2 g of benzyltriethylammonium bromide was stirred for 6 h at 35–55 °C. The potassium bromide formed was filtered off and dissolved in water leaving 0.5 g of polymeric material. Acidification of the aqueous filtrate precipitated 2,5-dimercapto-1,3,4-thiadiazole equivalent to 17 g of the starting salt indicating 83% conversion. The bromochloromethane was removed in vacuo from the organic filtrate leaving a thick liquid which was extracted with 1 L of anhydrous ether. The ether was removed in vacuo leaving 71.0 g (78% yield) of the title compound as a white solid, mp 60–61 °C. Recrystallization from ether gave crystals with mp 64–65 °C.

Anal. Calcd for $C_4H_4Cl_2N_2S_3$: C, 19.40; H, 1.63; Cl, 28.70; N, 11.34; S, 39.90. Found: C, 19.90; H, 1.72; Cl, 28.50; N, 11.63; S, 39.20.

**3,5-Bis[(chloromethyl)thio]-4-cyanoisothiazole (6).** In a 500-mL flask equipped with a reflux condenser, a mechanical stirrer, and a thermometer were placed 10.90 g (0.05 mol) of the disodium salt of 4-cyano-3,5-dimercaptoisothiazole (**5**) and 300 mL of bromochloromethane. To this slurry, 0.44 g of benzyltriethylammonium bromide was added, and the reaction mixture was heated at 24–55 °C for 5 h. The reaction mixture was filtered to remove the sodium bromide produced, and the bromochloromethane was removed in vacuo from the filtrate leaving a tan solid. The solid was extracted with hot ether, and the ether solution was concentrated in vacuo to give 6.00 g of the title compound as a light yellow powder, mp 92–93 °C. Further concentration gave an additional 2.10 g, mp 88–89 °C (total yield, 60%).

Anal. Calcd for $C_6H_4Cl_2N_2S_3$: C, 26.57; H, 1.48; N, 10.33; S, 35.47. Found: C, 26.80; H, 1.73; N, 10.46; S, 36.18.

**Registry No.**—3 2K, 4628-94-8; **4**, 62601-22-3; **5** 2Na, 2076-67-7; **6**, 62653-99-0; bromochloromethane, 74-97-5.

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(2) A. Senning and S. O. Lawesson, *Acta Chem. Scand.*, **16**, 117 (1962).
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(6) All melting points and boiling points are uncorrected. All new compounds gave satisfactory elemental analyses and displayed infrared and NMR spectra which were in agreement with the assigned structures.

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# Electronic Effects in Multicenter Rearrangements of Compounds with Nitrogen–Nitrogen Bonds

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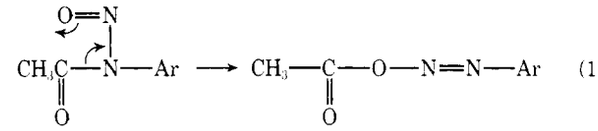
*Received September 10, 1976*

Huisgen and co-workers[1] and Hey and co-workers[2] have shown that the rates of rearrangements of *N*-nitroso amides **1** (eq 1) are but slightly influenced by either electron-withdrawing or electron-donating substituents.



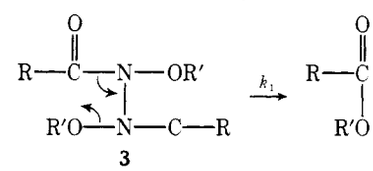
**1** **2** (1)

A plot of rate data reported by these authors against Hammett $\sigma^+$ [4] constants shows some scattering of points but the best straight line has a slope of zero. Likewise we have measured the rates of rearrangement of *N*-nitroso-*N*-cyclohexylbenzamides, and found little effect from placing either electron-donating or electron-withdrawing substituents on the aromatic ring. These data have been interpreted as being consistent with a multicenter process[1,2] rather than an ionic process. In a multicenter process involving simultaneous bond breaking and bond formation, the influence of electron-donating and electron-withdrawing substituents would be conflicting.

We wanted to see if electronic effects on the decomposition of **3** by a multicenter process would likewise be confusing.

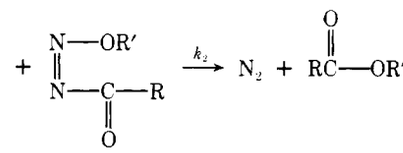
Previous work[3] has shown that the spontaneous reaction of **3a** in refluxing methanol or benzyl alcohol at room temperature occurred by a concerted process, while reaction in refluxing benzyl alcohol or with added acid occurred with the generation of a free acylium ion.

Scheme I



**3**

3a, R = $CH_3$; R′ = $NC_3H_7$
b, R = $XC_6H_4$; R′ = $C_6H_5CH_2$
c, R = $CH_3$; R′ = $XC_6H_4CH_2$



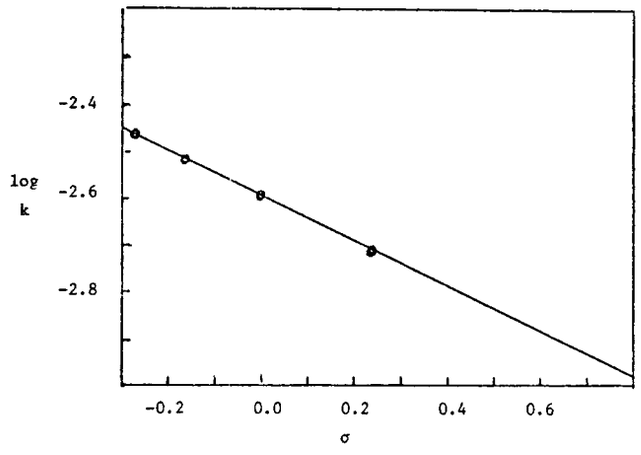



**Figure 1.** Log $k$ vs. $\sigma$ for $N,N'$-di-$p$-X-benzoyl-$N,N'$-dibenzyloxyhydrazines in chloroform at 30.1 ± 0.1 °C, $p = -0.47$.

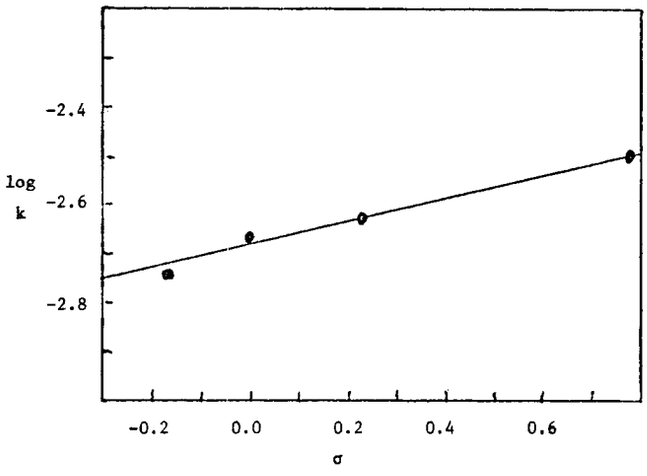



**Figure 2.** Log $k$ vs. $\sigma$ for $N,N'$-diacetyl-$N,N'$-di-$p$-X-benzyloxyhydrazines in chloroform at 59.4 ± 0.3 °C, $p = 0.22$.

Electron-donating substituents on R in **3b** with electron-withdrawing substituents on R′ in **3c** were found to accelerate the rates of reaction. Plots of log $k$ vs. $\sigma$ (Figures 1 and 2) for the two series of compounds **3b** and **3c** showed straight lines and $\rho$ values of −0.47 and +0.22 were calculated, respectively. These indicate the expected stabilization of incipient alkoxide anions and acylium ions of the transition state.

## Experimental Section

Melting points were determined using a Thomas-Hoover Uni-melt capillary apparatus and are corrected. Visible absorption spectra were measured with a Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer or a Beckman DU spectrophotometer. Molecular weights were determined with a Hitachi Perkin-Elmer molecular weight apparatus, Model 115.

**Preparation of Amides.** Amides were prepared by the method of White.[4] Previously unknown amides included $N$-cyclohexyl-$m$-chlorobenzamide, mp 121 °C, $N$-cyclohexyl-$m$-methylbenzamide, mp 121 °C, and $N$-cyclohexyl-$m$-nitrobenzamide, mp 146 °C.[5]

***N*-Nitroso-*N*-cyclohexyl-Substituted Benzamides.** The procedure described by Huisgen and Kraus[16] was used to prepare the nitroso amides. Solutions of these nitroso amides in carbon tetrachloride were prepared and held in a constant temperature bath at 25.0 ± 0.01 °C. Samples were withdrawn and changes in the absorption at 430 nm were recorded. From these data the rates shown in Table I were calculated. Similarly rates of decomposition of $N$-nitroso-$N$-cyclohexyl-substituted benzamides in acetic acid were measured and the results are in Table II.

**Rate of Decomposition of *N,N'*-Diacyl-*N,N'*-dialkoxyhydrazines.** These unstable compounds were prepared by lead tetraacetate oxidation of $N$-acyl-$O$-alkylhydroxylamines as described before.[3] Solutions of initial concentration in the range $5 \times 10^{-2}$ to $5 \times 10^{-3}$ $m$ in chloroform were accurately prepared and kept in a constant temperature bath. Aliquots were withdrawn at 2-h intervals, and the molecular weights were measured using a Hitachi Perkin-Elmer molecular weight apparatus, Model 115. First-order rate constants were determined from the slope of the plot of $M_\infty - M_t$ against time.

**Table I. Rate Constants for Decomposition of *N*-Nitroso-*N*-cyclohexyl-Substituted Benzamides in Carbon Tetrachloride**

| Substituent | Constant, $s^{-1}$ | Substituent | Constant, $s^{-1}$ |
|---|---|---|---|
| $p$-$OCH_3$ | $3.0 \times 10^{-4}$ | $m$-$CH_3$ | $3.0 \times 10^{-4}$ |
| $m$-Cl | $3.5 \times 10^{-4}$ | H | $4.0 \times 10^{-4}$ |

**Table II. Rate Constants for Decomposition of *N*-Nitroso-*N*-cyclohexyl-Substituted Benzamides in Acetic Acid**

| Registry no. | Substituent | Constant, $s^{-1}$ |
|---|---|---|
| 62250-57-1 | $m$-$CH_3$ | $2.0 \times 10^{-3}$ |
| 62250-58-2 | $p$-Nitro | $5.36 \times 10^{-4}$ |
| 62250-59-3 | $m$-Chloro | $1.24 \times 10^{-3}$ |
| 62250-60-6 | $m$-Nitro | $9.39 \times 10^{-4}$ |
| 62250-61-7 | $p$-Methoxy | $1.39 \times 10^{-3}$ |
| 62250-62-8 | None | $1.73 \times 10^{-3}$ |

**Registry No.**—**3b** (X = $p$-$CH_3$), 62250-50-4; **3b** (X = H), 38636-07-6; **3b** (X = $p$-Cl), 62250-51-5; **3b** (X = $p$-$OCH_3$), 62250-52-6; **3c** (X = $p$-$OCH_3$), 53821-07-1; **3c** (X = H), 62250-53-7; **3c** (X = $p$-Cl), 62250-54-8; **3c** (X = $p$-$NO_2$), 62250-55-9; $N$-cyclohexyl-$m$-chlorobenzamide, 62250-56-0; $N$-cyclohexyl-$m$-methylbenzamide, 53205-66-6; $N$-cyclohexyl-$m$-nitrobenzamide, 2702-32-1.

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(5) Satisfactory microanalyses (0.3% absolute) were obtained on all new compounds.

# Synthetic Methods and Reactions. 35.[1] Regioselective Oxidation of Alkyl (Cycloalkyl) Methyl Ethers to Carbonyl Compounds with Nitronium Tetrafluoroborate

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*Received December 8, 1976*

In our previous work we have shown that nitrosonium salts oxidize benzylic alcohols and the trimethylsilyl and tributylstannyl derivatives of secondary alcohols to carbonyl compounds,[2] and cleave benzylic esters[3] with ease. We now wish to report a related study on the reaction of alkyl (cycloalkyl) methyl ethers with nitronium tetrafluoroborate leading to a facile, regioselective oxidative cleavage.

Contrary to the nitrosonium ion, nitronium ion generally does not act as a hydride acceptor. However, it is a better electrophile toward $\pi$, n, and $\sigma$ donors, as illustrated by, for example, aromatic nitration,[4] nitrate ester formation,[5] and

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