detail by Kice and Legan[7a] for following the kinetics of the reactions of nucleophiles with phenyl α-disulfone. Reactions of 8 were followed at 313 nm, while those of 7 were followed at whatever wavelength in the 320–335-nm range had been shown by preliminary experiments to lead to the largest change in absorbance. The reactions of phenyl α-disulfone with the cyclic tertiary amines were followed at 255 nm in the case of both Dabco and quinuclidine and at 245 nm in the case of 3-quinuclidinol. The spontaneous hydrolysis of 7 at elevated temperatures was followed using the same type of procedure employed[7c] to follow the spontaneous hydrolysis of phenyl α-disulfone.

Thermochemistry of the Alkaline Hydrolysis of 7. The experimental procedures used for the calorimetric measurements on the heat of alkaline hydrolysis of 7 were the same as those previously described[9] for studying the heat of alkaline hydrolysis of phenyl α-disulfone.

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Registry No.—9, 10409-06-0.

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Reaction of Cyanide and Sulfite Ions with Oxidized Derivatives of Dibenzo[*ce*]-1,2-dithiin and Naphtho[1,8-*cd*]-1,2-dithiole

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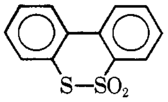
The cyclic thiolsulfonates dibenzo[*ce*]-1,2-dithiin 1,1-dioxide (1) and naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide (4) react rapidly in aqueous dioxane with excess cyanide or sulfite to undergo opening of the thiolsulfonate ring with formation (from reaction with CN^-) of thiocyanates (8 and 10, respectively) and (from sulfite) Bunte salts (7 and 9). Acidification of the final reaction solutions with carboxylic acid buffers of appropriate pH leads to rapid reversal of the ring-opening reactions and quantitative regeneration of 1 or 4 (Schemes I–IV). Surprisingly, in the regeneration of the cyclic thiolsulfonates from the thiocyanates or Bunte salts the CN group in each thiocyanate is displaced by $-SO_2^-$ about 30 times faster than the $-SO_3^-$ group in the analogous Bunte salt, thereby showing that in certain circumstances thiocyanates can be better sulfenylating agents than the analogous Bunte salt. Kinetic and equilibrium measurements on the various reactions show that the equilibrium constants for opening of the six-membered thiolsulfonate ring in 1 are about 20 times larger than those for opening the five-membered thiolsulfonate ring in 4, even though the *rates* of ring opening for 4 are faster in each case by a factor of about 10. While the analogous cyclic α-disulfones 3 and 6 react with sulfite and cyanide to undergo opening of the α-disulfone ring, acidification of the final reaction solution does not lead to regeneration of the α-disulfone. Reasons for this difference in behavior from that found with thiolsulfonates 1 and 4 are presented. Cyclic sulfinyl sulfone 2, dibenzo[*ce*]-1,2-dithiin 1,1,2-trioxide, reacts rapidly and quantitatively with sulfite ion to give a Bunte salt *S*-oxide (16). In acetate or chloroacetate buffers 16 decomposes to regenerate 2, which then undergoes rapid hydrolysis to diphenyl-2,2′-disulfinate (17). In more acid buffers 16 undergoes an extremely rapid acid-catalyzed decomposition that leads to cyclic thiolsulfonate 1 via the mechanism shown in Scheme V.

As part of a general study of the reaction of nucleophiles toward oxidized derivatives of dibenzo[*ce*]-1,2-dithiin (compounds 1–3) and naphtho[1,8-*cd*]-1,2-dithiole (compounds 4–6) we have examined the reaction of cyanide ion and sulfite ion with the majority of these substrates. We find that the reaction of these two nucleophiles with the various substrates exhibits interesting, informative, and, in some cases, rather unexpected variations in behavior with both substrate and nucleophile. For example, with certain of the substrates, *but not with others*, opening of the ring by cleavage of the sulfur–sulfur bond through nucleophilic attack of sulfite or cyanide on one of the sulfurs can be readily and quantitatively



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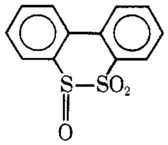

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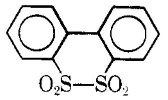

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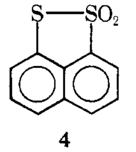

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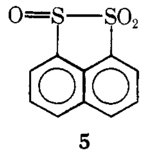

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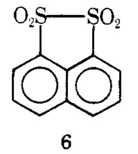

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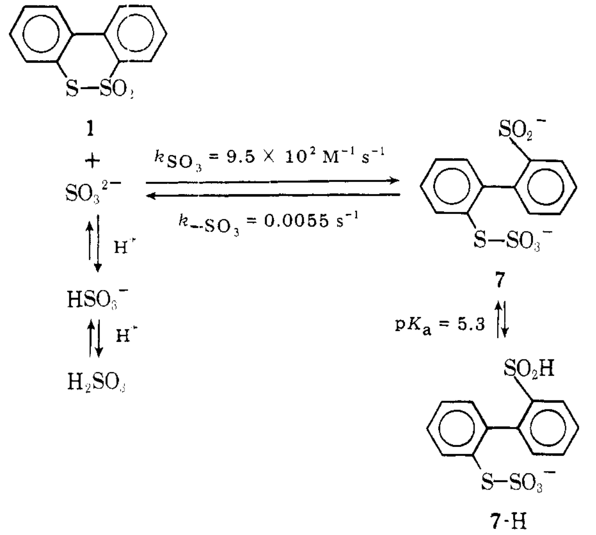
Scheme I. Reaction of Sulfite with Dibenzo[*ce*]-1,2-dithiin 1,1-Dioxide in 60% Dioxane at 25 °C



$$K_{eq} = (k_{SO_3}/k_{-SO_3}) = 1.7 \times 10^5\ M^{-1}$$

reversed by an appropriate change in the pH of the reaction solution. Surprisingly, in re-forming thiolsulfonates 1 or 4 from the ring-opened structures we find that CN^- is displaced considerably more rapidly from an -SCN group by $-SO_2^-$ than is SO_3^{2-} from $-SSO_3^-$.

Our observations on these and other aspects of the reaction of cyanide and sulfite with 1–6 form the subject of this paper.

Results and Discussion

Reaction of Sulfite and Cyanide with Dibenzo[*ce*]-1,2-dithiin 1,1-Dioxide (1). At 25 °C in 60% dioxane as solvent dibenzo[*ce*]-1,2-dithiin 1,1-dioxide (1) reacts rapidly with excess sulfite ion to cleave the sulfur–sulfur bond in 1 and form Bunte salt 7 (Scheme I). The reaction can be followed by monitoring the disappearance of the absorption maximum due to 1 at 296 nm by stopped-flow spectrophotometry. As can be seen from Table I, the experimental first-order rate constant for the disappearance of 1 is proportional to sulfite concentration. From $k_1/[SO_3^{2-}]$ the second-order rate constant for the reaction of SO_3^{2-} with 1 (k_{SO_3} in Scheme I) is found to be $9.5 \times 10^2\ M^{-1}\ s^{-1}$.

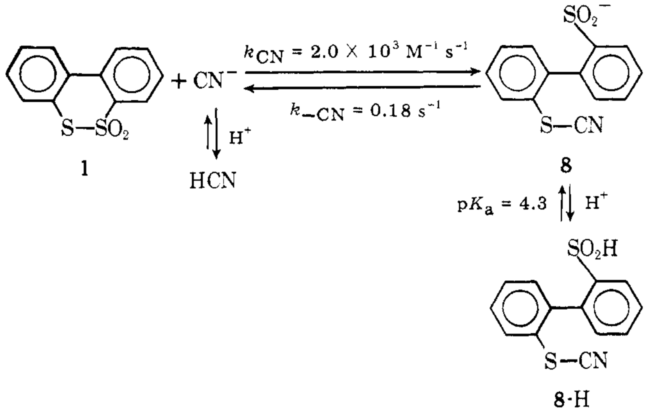
Thiolsulfonate 1 also reacts rapidly with excess cyanide (1:1 CN^-/HCN buffer) to undergo ring opening to thiocyanate 8 (Scheme II). The kinetic data for the reaction, which can be followed in the same way as the 1-sulfite reaction, are also listed in Table I, and from $k_1/[CN^-]$ the second-order rate constant for the reaction of cyanide with 1 (k_{CN} in Scheme II) is $2.0 \times 10^3\ M^{-1}\ s^{-1}$.

If either Bunte salt 7 (Scheme I) or thiocyanate 8 (Scheme II) is treated with a buffer of sufficient acidity to completely protonate SO_3^{2-} to HSO_3^- or CN^- to HCN, but not one so acid as to protonate too extensively the $-SO_2^-$ group of either 7 or 8, then both Bunte salt 7 and thiocyanate 8 revert back readily and quantitatively to 1 (reactions k_{-SO_3} of Scheme I and k_{-CN} of Scheme II) via displacement of, respectively, the $-SO_3^-$ group of the Bunte salt and the CN group of the thiocyanate, by the sulfinate ion function present in either 7 or 8. The kinetic behavior of the reversion of 7 or 8 to 1 is outlined in the following paragraphs.

Table I. Kinetics of the Reaction of Excess Sulfite or Cyanide with Dibenzo[*ce*]-1,2-dithiin Dioxide in 60% Dioxane at 25 °C

$10^4[1]_0$, M	$10^3[SO_3^{2-}]$, M	$[CN^-] = [HCN]$, M	k_1, s^{-1}	$k_1/[SO_3^{2-}]$, $M^{-1}\ s^{-1}$	$k_1/[CN^-]$, $M^{-1}\ s^{-1}$
1.0	4.0		3.7	9.3×10^2	
	8.0		7.7	9.6×10^2	
		0.02	39.4		2.0×10^3
		0.01	20.1		2.0×10^3

Scheme II. Reaction of Cyanide with Dibenzo[*ce*]-1,2-dithiin 1,1-Dioxide in 60% Dioxane at 25 °C



$$K_{eq} = (k_{CN}/k_{-CN}) = 1.1 \times 10^4\ M^{-1}$$

Thiolsulfonate 1 (10^{-4} M) was treated with excess cyanide ($[CN^-] = 5 \times 10^{-4}$ M), and after the reaction of 1 with CN^- to give 8 was complete, as evidenced by no further decrease in the absorbance at 296 nm, the solution was acidified by the injection of a small amount of a concentrated solution of chloroacetic acid/sodium chloroacetate buffer sufficient to give a final chloroacetic concentration in the range 0.01–0.02 M and a chloroacetate concentration of 0.01 M. The increase in the absorbance of the solution at 296 nm was then followed, and after a few minutes not only had the absorbance at 296 nm returned to the value expected for a 10^{-4} M solution of 1 but also the complete spectrum was identical with that of thiolsulfonate 1. A plot of log ($A^{296}_\infty - A^{296}$) vs. time for each run showed excellent linearity; the slopes of these plots gave k_{-1} (the experimental first-order rate constant for the reversion of 8 to 1).

In 60% dioxane a 1:1 $ClCH_2COO^-/ClCH_2COOH$ buffer has pH 5.48.[1] Unpublished work in this laboratory[2] indicates the pK_a for benzenesulfinic acid in 60% dioxane is between 4.2 and 4.3. The observed k_{-1}'s for the reversion of 8 to 1 as a function of buffer pH are [(pH of buffer), k_{-1}] (5.48) 0.17 and (5.18) 0.155 s^{-1}. An experiment in which the solution was acidified with 0.1 M $HClO_4$, rather than a chloroacetate buffer, showed that regeneration of 1 from the thiocyanate, while eventually complete, was orders of magnitude slower than in the chloroacetate buffer. This shows that the $-SO_2H$ group in 8-H is very unreactive relative to the $-SO_2^-$ group in 8 insofar as performing the displacement of the CN group from the thiocyanate function. The actual value of k_{-CN} in Scheme II is therefore related to the measured k_{-1}'s by eq 1, where K_a is

$$k_{-CN} = k_{-1}\left[\frac{K_a}{K_a + a_{H^+}}\right] \qquad (1)$$

the acid dissociation constant for 8-H in 60% dioxane. Assuming that the pK_a for 8-H is essentially the same as that[2] for $PhSO_2H$ (4.3) gives a calculated k_{-CN} which is independent of pH and has a value of 0.18 s^{-1}. From this value and that for k_{CN} determined earlier, $K_{eq} = (k_{CN}/k_{-CN})$ is equal to $1.1 \times 10^4\ M^{-1}$.

To check on the correctness of this value of K_{eq} we also carried out an experiment in which small increments of cyanide (as a 1:1 CN^-/HCN buffer) were added to a 10^{-4} M solution of 1 in 60% dioxane and the final equilibrium absorbance at 296 nm after the addition of each increment was measured. From these data, the absorbance at 296 nm in the

Table II. Kinetics of the Reaction of Excess Sulfite or Cyanide with Naphtho[1,8-*cd*]-1,2-dithiole 1,1-Dioxide in 60% Dioxane at 25 °C

$10^4[4]_0$, M	$10^3[SO_3^{2-}]$, M	$[CN^-] = [HCN]$, M	k_{exptl}, s^{-1}
2.0	2.0		24
	4.0		51
0.5		0.0025	76[a]

[a] Average of several runs; rates reproducible to ±3%.

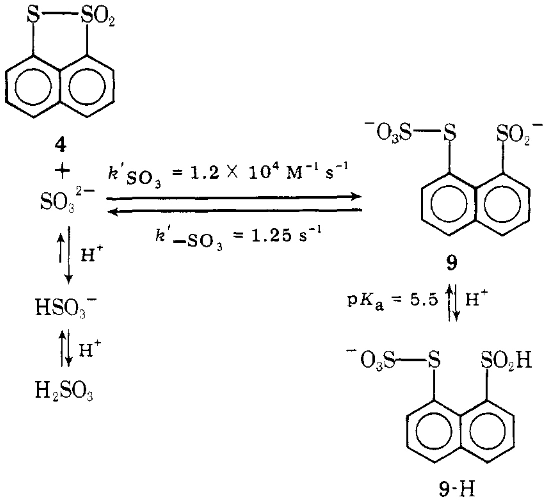
absence of added cyanide and the absorbance at this wavelength when sufficient excess CN^- has been added to convert **1** completely to **8**, one can calculate values of K_{eq}. We obtained $1.05 \pm 0.08 \times 10^4$ M^{-1}, in excellent agreement with the value estimated from the rates of the forward and reverse reactions.

The reversion of Bunte salt **7** to **1** was studied kinetically in the same way as the reversion of **8** to **1**, i.e., after the reaction of **1** (10^{-4} M) with 5×10^{-4} M sodium sulfite, the solution was acidified by addition of a small amount of concentrated chloroacetate buffer and the increase in optical density at 296 nm was followed. Regeneration of **1** from **7** was quantitative and followed excellent first-order kinetics. The observed k_{-1}'s for the reversion of **7** to **1** as a function of buffer pH were [(pH of buffer), k_{-1}] (5.78) 0.00426, (5.48) 0.00324, and (5.17) 0.00234 s^{-1}. One sees that there is much more dependence of k_{-1} on the buffer pH than in the experiments with **8**. Apparently the $-SSO_3^-$ group exerts a very significant acid-weakening effect on the $-SO_2H$ group in **7**-H such that its pK_a is about 1.0-pK_a unit larger than that of **8**-H, and therefore a considerable fraction of **7** is protonated to **7**-H in the more acidic of the chloroacetate buffers. Using a value of 5.3 for the pK_a of **7**-H and the measured k_{-1}'s, the relation $k_{-SO_3} = k_{-1}(K_a/K_a + a_{H^+})$ gives a value for k_{-SO_3} which is independent of pH and equal to $5.5 \pm 0.1 \times 10^{-3}$ s^{-1}. From this and k_{SO_3}, $K_{eq} = (k_{SO_3}/k_{-SO_3})$ for the $SO_3^{2-} + 1 \rightleftarrows 7$ equilibrium is 1.7×10^5 M^{-1}.

The fact that k_{-CN} for **8** (intramolecular displacement of CN^- from $-SCN$ by $-SO_2^-$) is about 30 times *faster* than k_{-SO_3} for **7** (intramolecular displacement of SO_3^{2-} from $-SSO_3^-$ by $-SO_2^-$) is surprising, interesting, and unexpected since the impression gained from the literature[3,4] is that Bunte salts are generally considered to be more reactive sulfenylating agents than thiocyanates. To make sure that the greater ease of displacement of CN^- from $-SCN$ in **8** as compared to SO_3^{2-} from $-SSO_3^-$ in **7** was not due to some peculiarity unique to the dibenzo[*ce*]-1,2-dithiin system, we therefore felt it was important to investigate the rates of the forward and reverse reactions associated with the analogous equilibria involving sulfite and cyanide and the cyclic 5-membered thiolsulfonate, naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide (**4**). Such studies would have the additional bonus of indicating to what extent the equilibrium constants for ring opening were influenced by the change from **1** to **4**. Based on the behavior[13] of the equilibria involving the hydrolysis of the two cyclic sulfinyl sulfones **2** and **5** to their respective disulfinic acids, the change from **1** to **4** might be expected to lead to a sizeable decrease in K_{eq} for ring opening.

Reaction of Sulfite and Cyanide with Naphtho[1,8-*cd*]-1,2-dithiole 1,1-Dioxide (4). The reaction of **4** with either excess sulfite or excess cyanide (1:1 CN^-/HCN buffer) can be followed by stopped-flow spectrophotometry at 304 nm. The experimental first-order rate constants for the various runs are given in Table II. Because, as will become evident shortly, the rates of reverse reactions (k'_{-SO_3} in Scheme III and k'_{-CN} in Scheme IV) are much faster relative to the rates of the forward reactions than in the case of **1**, it turns out that under the conditions in Table II, particularly for cyanide, the reactions do not go entirely to completion, and so k_{exptl} for each run is actually equal to $(k'_{Nu}[Nu^-] + k'_{-Nu})$ rather than to just $k'_{Nu}[Nu^-]$.[5] We will therefore defer calculation of k'_{SO_3} and k'_{CN} for **4** until after we have outlined the determination of k'_{-SO_3} and k'_{-CN} from the experiments outlined in the next several paragraphs.

Scheme III. Reaction of Sulfite with Naphtho[1,8-*cd*]-1,2-dithiole 1,1-Dioxide in 60% Dioxane at 25 °C

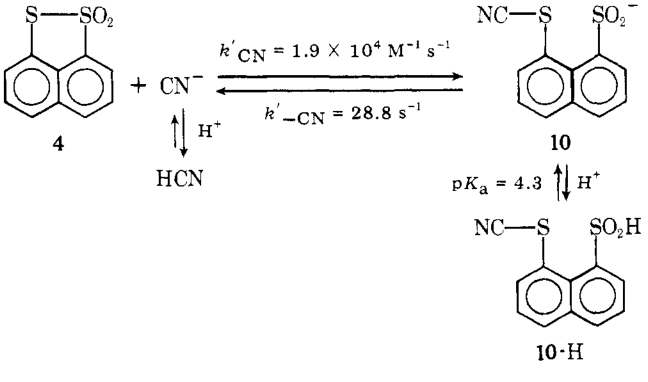


$K'_{eq} = (k'_{SO_3}/k'_{-SO_3}) = 9 \times 10^3$ M^{-1}

To determine the rate (k'_{-CN}) at which thiocyanate **10** (Scheme IV) reverts to **4** a solution prepared from **4** (2×10^{-4} M) and a 1:1 CN^-/HCN buffer containing $[CN^-] = 0.002$ M was placed in one of the reservoir syringes of a stopped-flow spectrophotometer and a chloroacetate buffer of appropriate pH was placed in the other syringe. The two solutions were then mixed, and the increase in the absorbance of the solution at 304 nm as **4** was regenerated from **10** was monitored. Good first-order kinetics were observed, and the experimental first-order rate constants were [(pH of buffer), k_{-1}] (5.48) 27.1 and (5.18) 25.4 s^{-1}. These measured k_{-1} values and an assumed pK_a for **10**-H of 4.3 (the same value as used for **8**-H) give a value of k'_{-CN} which is independent of pH and equal to 28.8 ± 0.1 s^{-1}. The value of k'_{CN} for the reaction of CN^- with **4** can then be calculated from this value of k'_{-CN} and k_{exptl} for cyanide in Table II: $k'_{CN} = (k_{exptl} - k'_{-CN})/[CN^-] = 1.9 \times 10^4$ M^{-1} s^{-1}. From the values of k'_{CN} and k'_{-CN}, K_{eq} for the $4 + CN^- \rightleftarrows 10$ equilibrium is equal to 6.6×10^2 M^{-1}.

Rate constant k'_{-SO_3} for reversion of Bunte salt **9** (Scheme III) to **4** was determined from similar experiments in which a solution prepared from 2×10^{-4} M **4** plus 4×10^{-3} M sodium sulfite was mixed with chloroacetate buffers of varying pH in

Scheme IV. Reaction of Cyanide with Naphtho[1,8-*cd*]-1,2-dithiole 1,1-Dioxide in 60% Dioxane at 25 °C



$K'_{eq} = (k'_{CN}/k'_{-CN}) = 6.6 \times 10^2$ M^{-1}

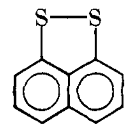
a stopped-flow spectrophotometer, and the regeneration of **4** from **9** followed. The experimental first-order rate constants were [(pH of buffer), k_{-1}] (5.78) 0.85, (5.48) 0.62, and (5.17) 0.39 s^{-1}. The sizeable decline in k_{-1} with decreasing pH shows, as was true earlier for Bunte salt **7**, that a considerable fraction of **9** is protonated to **9**-H in the more acidic chloroacetate buffers. If one assumes that the pK_a of the $-SO_2H$ group in **9**-H is 5.5 (or 0.2-pK_a unit larger than that for **7**-H), then k'_{-SO_3} as calculated from $k_{-1}(K_a/K_a + a_{H^+})$ is independent of pH and has a value of 1.25 ± 0.02 s^{-1}. Using this value of k'_{-SO_3} and the values of k_{exptl} for the reaction of sulfite with **4** in Table II, $k'_{SO_3} = (k_{exptl} - k'_{-SO_3})/[SO_3^{2-}] = 1.18 \pm 0.04 \times 10^4$ M^{-1} s^{-1}. This gives $K_{eq} = (k'_{SO_3}/k'_{-SO_3}) = 9 \times 10^3$ M^{-1} for the **4** + $SO_3^{2-} \rightleftarrows$ **9** equilibrium.

Comparison of the rate and equilibrium constants for the equilibria involving **4** (Schemes III and IV) with those for the equilibria involving **1** (Schemes I and II) reveals the following points of significance. First, as we had suspected might be the case, the equilibrium constants (K'_{eq}) for opening of the thiolsulfonate ring in **4** are about 20 times smaller in each instance than the equilibrium constants for the analogous ring-opening reactions involving **1**. Notice that this occurs even though the rate constants for the opening of the thiolsulfonate ring in **4** (k'_{SO_3} and k'_{CN}) are about 10 times faster for each nucleophile than for their analogous reaction (k_{SO_3} or k_{CN}) with **1**. The reason that both equilibrium constants for **4** are smaller than the analogous K_{eq}'s for **1** is that re-formation of the thiolsulfonate ring from **9** and **10** (k'_{-SO_3} and k'_{-CN}, respectively) is in each instance about 200 times faster than the corresponding reaction of **7** (k_{-SO_3}) or **8** (k_{-CN}). That both (k'_{-SO_3}/k_{-SO_3}) and (k'_{-CN}/k_{-CN}) should be of this large magnitude is not surprising. To go from **7** or **8** to the transition-state geometry necessary for the displacement reactions leading to **1** undoubtedly involves a significantly larger loss of rotational freedom (and therefore less favorable $\Delta G^{\ddagger}$) than to go from **9** or **10** to the transition-state geometry for the reactions leading to **4**.

The second point of particular significance is that, just as was true for **7** and **8**, we also find here that k'_{-CN} for **10** is about 25 times larger than k'_{-SO_3} for **9**. In other words, in this system, just as in the one derived from **1**, one again finds that $-SO_2^-$ can displace CN^- from $-SCN$ considerably more readily than it can displace SO_3^{2-} from $-SSO_3^-$. These results clearly demonstrate that a thiocyanate group can be more reactive as a sulfenylating agent than a Bunte salt under appropriate reaction conditions, a fact that does not seem to have been recognized previously. Notice that the present reaction conditions are such that, as soon as either SO_3^{2-} or CN^- is displaced, it is removed from further participation by protonation to either nonnucleophilic (HCN, H_2SO_3) or weakly nucleophilic (HSO_3^-) species.

At the same time one should recognize that the intramolecular character of the displacements involving $-SO_2^-$ and $-SCN$ in **8** and **10** makes these reactions many orders of magnitude faster than, for example, the corresponding intermolecular displacement by $PhSO_2^-$ on PhSCN, i.e., $PhSO_2^- + PhSCN \rightarrow PhSO_2SPh + CN^-$. Thus we found that, although some thiolsulfonate was formed on heating a solution containing 0.1 M $PhSO_2Na$ and 0.1 M PhSCN in a (1:1) chloroacetate buffer in 60% dioxane at 60 °C for 90 h, the yield was much too low to make the process of any synthetic value, and about 60% of the phenyl thiocyanate was recovered unreacted.

One other point regarding the reaction of cyanide with **4** is worth discussion. According to Tamagaki, Hirota, and Oae,[7] thiolsulfonate **4** when treated with 2 mol of cyanide in methanol at room temperature for 2 days gives the corresponding cyclic disulfide, naphtho[1,8-*cd*]-1,2-dithiole (**11**), in 72% yield, plus an undetermined amount of sodium cyanate. To determine to what extent and how rapidly thiocyanate **10**, proposed by Oae and co-workers[7] as the initial intermediate in their reaction, goes to disulfide **11** under our reaction conditions, 60% dioxane and a 1:1 CN^-/HCN buffer, we treated **4** (10^{-4} M) with a large excess of cyanide ($[CN^-] = [HCN] = 0.016$ M) and observed the ultraviolet spectrum of the solution over a period of 1 week at room temperature. While we did see the gradual appearance of measurable absorption at 368 nm, where disulfide **11** has a strong maximum (ϵ 13 200), its rate of appearance was very slow, and even after 7 days the amount of **11** formed corresponded to only about 25% of the amount of **4** originally present. To measure the amount of **10** remaining at that point, the reaction solution was acidified by the addition of excess chloroacetate buffer. Although some **4** was thereby regenerated, the amount was small enough to show that most of the thiocyanate had indeed reacted further by the end of 7 days, even though only about 25% had been transformed to disulfide. The spectrum suggested that a considerable amount of thiolsulfinate **12** was present after acidification of the reaction solution.



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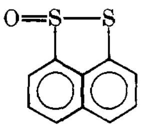


12

It is clear that under our reaction conditions the transformation of **10** to **11** is much slower than reported by Oae.[7] This may have its origin in the fact that our reaction medium is a 1:1 CN^-/HCN buffer rather than the considerably more basic solution of sodium cyanide in methanol used by Oae and coworkers. We hope to explore the slow transformation of **10** to **11** more carefully in the future. In any event, one should, of course, realize that it is *orders of magnitude* slower than the very rapid forward and reverse steps of the **4** + $CN^- \rightleftarrows$ **10** equilibrium that have been the principal object of our attention in the present work.

Tamagaki, Hirota, and Oae[7] also suggested that the rate constant for opening of the thiolsulfonate ring in **4** by cyanide (k'_{CN}) was probably *much slower than the rate of reaction of* cyanide with phenyl benzenethiolsulfonate (eq 2). The rate constant for eq 2 has been measured by Kice, Rogers, and Warheit[8] at 25 °C in 60% dioxane, and one sees that it is actually about two times *slower* than k'_{CN} for **4** and *not* many *times faster* as suggested by Oae.[7]

$$CN^- + PhS\text{-}SO_2Ph \xrightarrow{k_2 = 7.8 \times 10^3\ M^{-1}\ s^{-1}} PhSCN + PhSO_2^- \quad (2)$$

Reaction of Sulfite and Cyanide with Dibenzo[*ce*]-1,2-dithiin 1,1,2,2-Tetraoxide (3) and Naphtho[1,8-*cd*]-1,2-dithiole 1,1,2,2-Tetraoxide (6). Having found that the opening of the thiolsulfonate ring in either **1** or **4** by either sulfite or cyanide ion can be readily and quantitatively reversed by acidifying the reaction solution with a buffer of appropriate pH, we were naturally curious as to whether or not similar reversal of the opening of the ring would be possible with more highly oxidized derivatives of dibenzo[*ce*]-1,2-dithiin and naphtho[1,8-*cd*]-1,2-dithiole.

Cyclic α-disulfones **3** and **6** react quite readily with excess cyanide, and the course of the reactions can be conveniently followed spectrophotometrically. The reaction of **3** with excess sulfite can be followed similarly. The disappearance of the α-disulfones in all cases follows good first-order kinetics. Both the experimental first-order rate constants, k_1, and the second-order rate constants, as calculated from either $k_1/[CN^-]$ or $k_1/[SO_3^{2-}]$, are tabulated in Table III. The second-order rate constants are not too greatly different from those found for the reaction of phenyl α-disulfone, $PhSO_2SO_2Ph$, with the

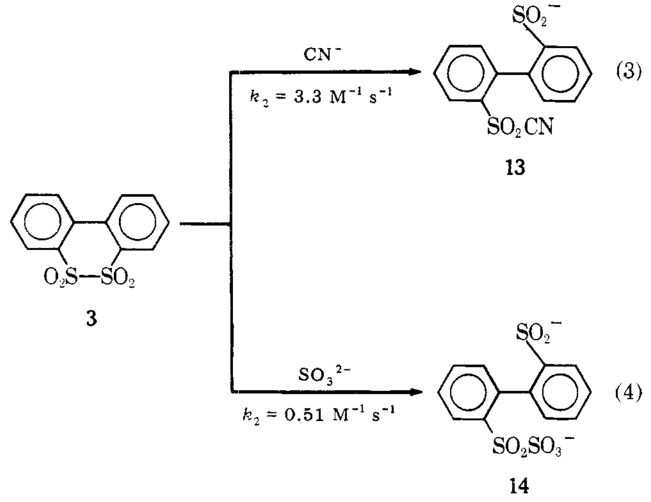
Table III. Kinetics of the Reaction of Excess Cyanide or Sulfite with Cyclic α-Disulfones 3 and 6 in 60% Dioxane at 25 °C

α-Disulfone, concentration (M)	$[CN^-] = [HCN]$, M	$[SO_3^{2-}]$, M	$k_1 \times 10^2$, s^{-1}	$k_1/[CN^-]$, $M^{-1} s^{-1}$	$k_1/[SO_3^{2-}]$, $M^{-1} s^{-1}$
3, 1.4×10^{-4}	0.04		14.0	3.5	
	0.02		6.8	3.4	
1.0×10^{-4}	0.001		0.31	3.1	
6, 1.0×10^{-4}	0.008		6.24	7.8	
	0.004		3.24	8.1	
3, 1.0×10^{-4}		0.01	0.51		0.51
		0.005	0.25		0.50

same nucleophiles under the same conditions (CN^-,[9a] 0.45 $M^{-1} s^{-1}$; SO_3^{2-},[9b] 1.0 $M^{-1} s^{-1}$).

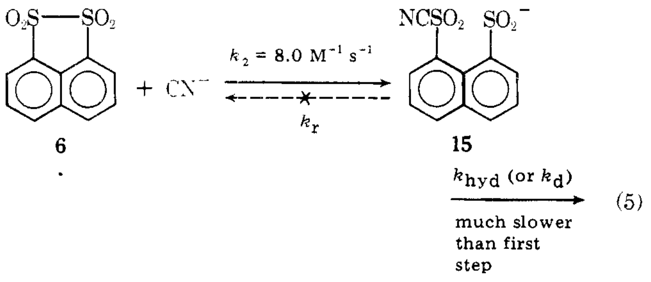
In marked contrast to the type of behavior observed with the systems derived from thiolsulfonates **1** and **4**, acidification with a chloroacetate buffer of the final reaction solution from the reaction of either **3** or **6** with cyanide or sulfite does *not* lead to any regeneration of **3** or **6**.

The failure to re-form any α-disulfone on acidification of the reaction solutions could be due to either of two causes. The first possibility is that the intermediates (**13**, **14**, and **15**) formed on the reaction of the cyclic α-disulfones with cyanide (eq 3 and 5) or sulfite (eq 4) are all quite unstable and break down or hydrolyze so rapidly that there is effectively none of the intermediate left by the time the initial reaction between the α-disulfone and the nucleophile is complete and the solution is acidified with the chloroacetate buffer. The alternative is that the intermediate is sufficiently stable to still be present in significant concentration when the solution is acidified but that the conversion of the intermediate back to the cyclic α-disulfone (step k_r in eq 5, for example) simply has too slow a rate to be able to compete with even a relatively slow decomposition (or hydrolysis) of the intermediate. In the case of the reactions involving **3**, the spectral behavior of the reaction solutions does not provide any clue as to which explanation is right, but in the case of the reaction of cyanide with α-disulfone **6** (eq 5) it is possible to state unequivocally that it is the second alternative which is the correct one.



(3)

(4)



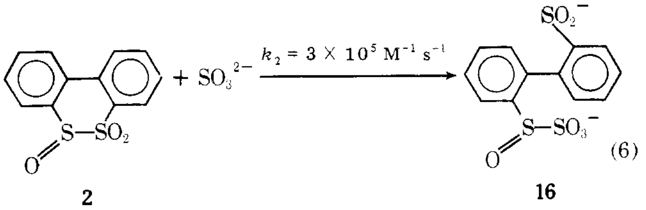
(5)

Table IV. Kinetics of the Reaction of Excess Sulfite Ion with Dibenzo[*ce*]-1,2-dithiin 1,1,2-Trioxide in 60% Dioxane at 25 °C

$10^4[\mathbf{2}]_0$, M	$10^3[SO_3^{2-}]$, M	k_1, s^{-1}	$k_1/[SO_3^{2-}]$, $M^{-1} s^{-1}$
0.75	0.75	2.4×10^2	3×10^5
	1.5	4.8×10^2	3×10^5

The initial reaction of **6** with cyanide to yield intermediate **15** is accompanied by a decrease in absorbance at 322 nm. This is then followed by a kinetically *much slower* second process that leads to a further significant decrease in the absorbance of the solution at 322 nm and which is associated with the decomposition (or hydrolysis) of **15**. In this case, then, the sequence of spectral changes definitely shows that the rate of disappearance of the intermediate is much slower than its rate of formation. The intermediate (**15**) is therefore present at a concentration comparable to the initial concentration of **6** when the reaction solution is acidified with the chloroacetate buffer. If upon acidification **15** were to revert to **6** at an appreciable rate (step k_r in eq 5), one would see an increase in the absorbance of the solution at 322 nm. However, what is actually observed is only the slow further decline in absorbance associated with the hydrolysis (or decomposition) of **15**. The first-order rate constant for the disappearance of **15** in the chloroacetate buffer is ~5×10^{-4} s^{-1}. Since k_r for **15** must be considerably slower than this, it cannot have a value larger than ~5×10^{-5} s^{-1} and, for the reasons outlined in a footnote,[10] is actually probably much smaller than this. Based on the behavior of **8** vs. **10**, one would expect k_r for **13** to be considerably slower than that for **15**. For this reason it seems reasonable to believe that in that system cyclization of **13** to **3** would have too slow a rate to be able to compete with other routes for the disappearance of **13** in the chloroacetate buffer.

Reaction of Sulfite Ion with Dibenzo[*ce*]-1,2-dithiin 1,1,2-Trioxide (2).[12] Cyclic sulfinyl sulfone **2** reacts extremely rapidly with sulfite ion in 60% dioxane. The reaction is accompanied by the disappearance of the maximum at 310 nm associated with **2** and the appearance of a new maximum at 280 nm (ε 6400) associated with the reaction product. Isolation of the reaction product and examination of its infrared spectrum show unequivocally that the product possesses a Bunte salt *S*-oxide functional group, $-S(O)SO_3^-$, and has structure **16** (eq 6). The kinetics of the reaction of **2** with excess sulfite are summarized in Table IV.



(6)

Upon acidification, solutions of Bunte salt *S*-oxide **16** exhibit behavior which varies in a striking manner with pH, as regards both the rate of disappearance of **16** and the reaction products. The rate and product data for the disappearance of **16** are given in Table V. Note that in each case where the rate has been determined in a buffer there is no dependence of rate on total buffer concentration. This shows that catalysis of the decomposition of **16** by either carboxylate ions or carboxylic acids is not a factor under our reaction conditions.

Examination of Table V reveals the following points: (1) although the rate of disappearance of **16** changes only very little on going from 1:1 acetate buffers (pH 7.44) to 1:1 chlo-

Table V. Kinetics of the Disappearance of Bunte Salt *S*-Oxide 16 in 60% Dioxane at 25 °C as a Function of pH

$10^4[16]_0$, M	Reaction conditions	pH	[RCOOH] = [RCOO⁻], M	$k_1 \times 10$, s^{-1} [a]	Major product
1.0	1:1 AcO⁻/AcOH buffer	7.44	0.02	0.0022	**17**
			0.01	0.0024	
			0.005	0.0022	
	1:1 chloroacetate buffer	5.48	0.02	0.004	**17**[b]
			0.01	0.003	
	1:1 dichloroacetate buffer	4.0	0.005	0.38	**1**
			0.0025	0.37	
	1:1 trifluoroacetate buffer	2.8	0.006	3.3	**1**
	0.01 M $HClO_4$	2.0		12	**1**

[a] In cases where the major reaction product is **1**, rates were followed by measuring the increase in absorbance at 296 nm (λ_{max} for **1**). In other cases, rates were followed by measuring the decrease in absorbance at 280 nm (λ_{max} for **16**). [b] Final spectrum suggests some **1** is also formed.

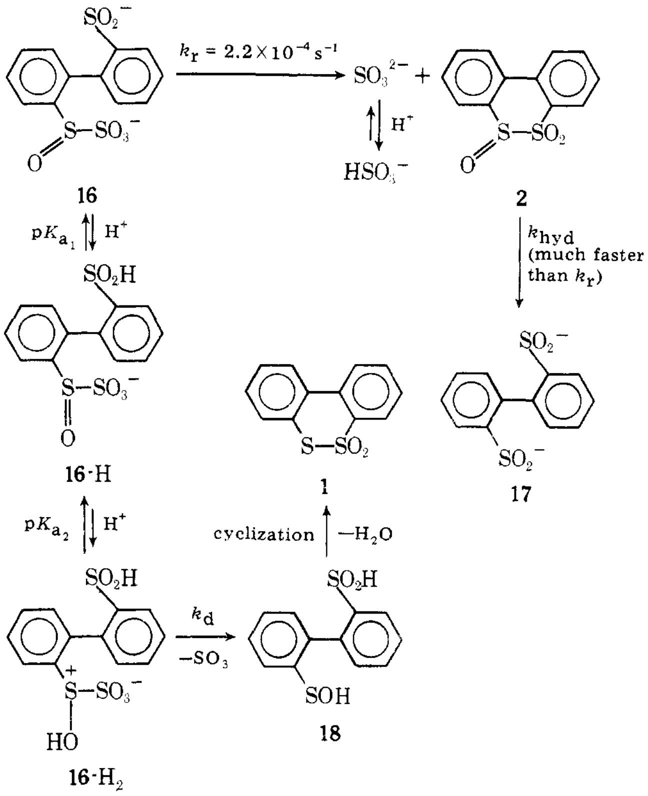
roacetate buffers (pH 5.48), it increases dramatically with further decreases in pH; (2) in those acid solutions in which it decomposes rapidly **16** yields cyclic thiolsulfonate **1** as the only important organic product; (3) on the other hand, in the acetate buffers no significant amount of **1** is formed, and from the spectrum of the solution at the end of the reaction (and the change that occurs if it is then acidified with perchloric acid) it appears that the major organic product is diphenyl-2,2′-disulfinate (**17**);[13] (4) in the chloroacetate buffer **17** is also an important product, but the final spectrum of the solution suggests that some **1** is formed too.

Before presenting the mechanistic scheme that will satisfactorily accommodate all of these various observations, it is important to mention that in separate experiments we found that cyclic sulfinyl sulfone **2** is hydrolyzed to **17** in a 1:1 acetate buffer ([AcO⁻] = 0.005 M) about 100 times faster (0.02 s^{-1}) than the rate of disappearance of **16** in the same medium.

Scheme V outlines what we believe are the mechanisms for the decomposition of Bunte salt *S*-oxide **16** under the different reaction conditions. Let us first consider the slow decomposition that occurs in the acetate buffers. We believe that this has as its rate-determining step the relatively slow reversion ($k_r = 2.2 \times 10^{-4}\ s^{-1}$) of **16** to sulfite ion and cyclic sulfinyl sulfone **2**. Since the hydrolysis of **2** to **17** in these buffers is much faster than k_r, the presence of **2** as an intermediate is not detectable spectrophotometrically. Sulfite ion is, of course, protonated to bisulfite as soon as it is formed, and this, plus the rather rapid rate of hydrolysis of **2** under these conditions, keeps the reverse of step k_r from becoming of any kinetic importance, even in the final stages of the reaction.[14] Earlier studies,[15,16] which have shown that aromatic sulfinates will react with reactive sulfinyl derivatives to form sulfinyl sulfones under conditions where they do not react with the analogous sulfonyl derivatives to give an α-disulfone, are consistent with the idea that **16** should be able to revert to **2** at a reasonable rate (just as **7** reverts to **1**) even though the equivalent intermediate **14** from the reaction of α-disulfone **3** with sulfite does not revert to **3** on acidification with a carboxylate buffer of appropriate pH.

Taking k_1 for the disappearance of **16** in a 1:1 acetate buffer as equal to k_r, one obtains a value of K_{eq} for the $2 + SO_3^{2-} \rightleftarrows 16$ equilibrium of $1.4 \times 10^9\ M^{-1}$, i.e., $K_{eq} = [k_2 \text{ (for eq 6)}/k_r]$. This is 10^4 times larger than the equilibrium constant for the $1 + SO_3^{2-} \rightleftarrows 7$ equilibrium. On a free energy basis this means that the opening of the sulfinyl sulfone ring in **2** by sulfite ion is 5.5 kcal/mol more favorable than the opening of the analogous thiolsulfonate ring in **1** by the same reagent.

Scheme V. Mechanism of Decomposition of Bunte Salt *S*-Oxide 16 in 60% Dioxane



Based on the behavior of the $1 + SO_3^{2-} \rightleftarrows 7$ equilibrium, one would expect that the rate of reversion of **16** to **2** plus sulfite ion would be independent of pH in carboxylic acid buffers until one reaches buffers of sufficient acidity to begin protonating **16** to its conjugate acid **16**-H. At that point the rate would begin to decrease with decreasing pH because the $-SO_2H$ group in **16**-H should be quite unreactive relative to the $-SO_2^-$ group in **16** insofar as performing the displacement of SO_3^{2-} from the Bunte salt *S*-oxide function.

Examination of Table V shows that, although the rate of disappearance of **16** is effectively independent of pH as the pH of the buffer is changed from 7.44 to 5.48, further decreases in pH lead *not* to a decrease but rather to a dramatic increase in rate. Clearly, then, a completely different mechanism for the disappearance of **16** becomes important as the acidity of the reaction medium is increased sufficiently, and this new mechanism leads to **1**, rather than **17**, as the organic product.

Given the pK_a of Bunte salt **7**, it seems reasonable to believe that the pK_a of the sulfinate group in **16** should be no less than about 5.0. Protonation of **16** to **16**-H should therefore be virtually complete at pH 4.0. The fact that the rate of disappearance of the Bunte salt *S*-oxide continues to increase markedly as the pH is lowered beyond this point shows that the rapid decomposition to **1** in acid solutions involves the addition of *more than just one proton* to **16**.

A straightforward and reasonable mechanism of this type for the acid-catalyzed decomposition of **16** is shown in Scheme V. It involves (a) the reversible protonation of the sulfinyl group in **16**-H to give **16**-H_2, (b) decomposition of **16**-H_2 by loss of sulfur trioxide to afford **18**, and (c) cyclization of this mixed sulfenic–sulfinic acid to give thiolsulfonate **1**. Formation of a thiolsulfonate by the reaction of an aromatic sulfenic acid with a sulfinic acid has been observed before.[2,17] The intramolecular nature of this reaction in the case of the conversion of **18** to **1** should allow it to occur particularly readily.

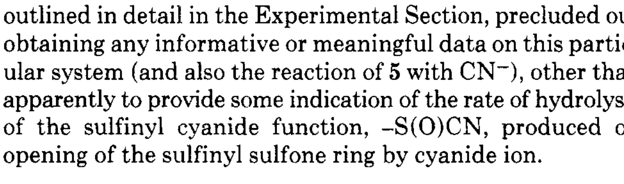
The pK_a of **16**-H_2, although unknown, is presumably less than 0. Given that, and assuming k_d to be rate determining, the mechanism for the acid-catalyzed decomposition of **16** shown in Scheme V predicts that the acid-catalyzed rate constant, k_{H^+}, under our reaction conditions will be given by eq 7. The mechanism therefore predicts that until $a_{H^+} > K_{a_1}$

$$k_{H^+} = \left[\frac{k_d}{K_{a_2}}\right]\left[\frac{a_{H^+}{}^2}{K_{a_1} + a_{H^+}}\right] \qquad (7)$$

the reaction should exhibit a greater than first-power dependence on a_{H^+}. That this is indeed the case is suggested by the fact that changing from a chloroacetate buffer of pH 5.48 to a dichloroacetate buffer of pH 4.00, an increase of a factor of 30 in a_{H^+}, leads to a greater than 100-fold increase in k_{H^+} (remember that the main contributor to the rate of decomposition of **16** in the chloroacetate buffer is still the reaction that leads to **17** rather than the acid-catalyzed decomposition to **1**).

Once $a_{H^+} \gg K_{a_1}$ the mechanism predicts that k_{H^+} should increase linearly with a_{H^+}. Inspection of the data for the pH range 2.0–4.0 in Table V shows that the actual increase in k_{H^+} is somewhat smaller than predicted from eq 7 and that the effect becomes more pronounced the lower the pH. We believe this is due to the fact that at higher acidities the cyclization of **18** to **1** becomes slower than k_{H^+}, with the result that the measured rate of formation of **1** becomes slower than predicted from eq 7.[18]

The mechanism in Scheme V for the acid-catalyzed decomposition of the Bunte salt *S*-oxide has considerable analogy to the mechanism[19] of the acid-catalyzed decomposition of an ordinary Bunte salt (eq 8). In eq 8 zwitterion **19**, rather **16**-H_2, undergoes loss of sulfur trioxide. When one compares the rates of the two acid-catalyzed decompositions under a given set of reaction conditions (0.01 M $HClO_4$ in 60% dioxane at 25 °C), one finds that the rate of decomposition of Bunte salt *S*-oxide **16** is a staggering 3×10^8 times *faster* than the rate of decomposition of the Bunte salt $PhSSO_3^-$. The Bunte salt *S*-oxide is thus over 10^8 times *less stable* in acid solution than an analogous Bunte salt. Presumably one of the major factors responsible for this is the much greater basicity of the sulfinyl group in the *S*-oxide as compared to the sulfide sulfur in the Bunte salt, i.e., K_{a_2} in Scheme V $\ll K'_a$ in eq 8;



$$C_6H_5{-}S{-}SO_3^- + H^+ \overset{K'_a}{\rightleftharpoons} C_6H_5{-}\overset{+}{\underset{H}{S}}{-}SO_3^- \xrightarrow{k'_d} C_6H_5{-}SH + SO_3 \quad (8)$$

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sulfinyl groups are known generally to be much more basic than equivalently substituted sulfide functionalities.[20]

We had also hoped to be able to study the reaction of cyanide ion with **2**. However, experimental difficulties, which are outlined in detail in the Experimental Section, precluded our obtaining any informative or meaningful data on this particular system (and also the reaction of **5** with CN^-), other than apparently to provide some indication of the rate of hydrolysis of the sulfinyl cyanide function, -S(O)CN, produced on opening of the sulfinyl sulfone ring by cyanide ion.

Experimental Section

Synthesis of Cyclic Thiolsulfonates, Sulfinyl Sulfones, and α-Disulfones. Dibenzo[*ce*]-1,2-dithiin 1,1-dioxide (**1**) and 1,1,2-trioxide (**2**) were prepared as described in a previous paper,[13] as was also naphtho[1,8-*cd*]-1,2-dithiole 1,1,2-trioxide (**5**). Naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide (**4**) was prepared following the procedure of Zweig and Hoffman.[22]

Dibenzo[*ce*]-1,2-dithiin 1,1,2,2-Tetroxide (3). Thiolsulfonate **1** (1.0 g, 4.0 mmol) was dissolved in 25 mL of chloroform, a solution of 1.8 g (8.9 mmol) of 85% *m*-chloroperbenzoic acid in 3.0 mL of the same solvent was added to it at room temperature, and the solution was stirred for 4 days. The white precipitate of **3** was removed by filtration. The filtrate was then extracted three times with 5% sodium bicarbonate to remove *m*-chlorobenzoic acid. It was then washed with water and dried over anhydrous magnesium sulfate. Concentration of the chloroform solution led to the precipitation of additional crops of **3**. The combined crops of **3** were recrystallized from chloroform/hexane to afford pure **3**, mp 244–245 °C dec, in 73% yield (0.83 g); IR (KBr) SO_2 absorptions at 1343 s, 1329 s, 1167 s, 1147 cm^{-1} ms; UV (60% dioxane) λ_{max} 313 nm (ϵ 6450).

Anal. Calcd for $C_{12}H_8S_2O_4$: C, 51.42; H, 2.88; S, 22.87. Found: C, 51.30; H, 2.99; S, 22.87.

Naphtho[1,8-*cd*]-1,2-dithiole 1,1,2,2-Tetroxide (6). A solution of 0.284 g of **4** in 10 mL of chloroform was mixed with a solution of 0.53 g of 85% *m*-chloroperbenzoic acid in 10 mL of the same solvent, and the mixture was stirred for 1 day at room temperature. The chloroform solution was then extracted three times with 5% sodium bicarbonate, washed once with water, and dried over $MgSO_4$, most of the chloroform removed under reduced pressure, and hexane added to precipitate α-disulfone **6**. The precipitate was recrystallized from chloroform/hexane, giving 0.15 g (46%) of pure **6**. The compound has no melting point but decomposes slowly on heating above 200 °C; IR (KBr) SO_2 absorptions at 1350, 1180, 1120 cm^{-1}; UV (60% dioxane) λ_{max} 302 nm (ϵ 6500).[23]

Anal. Calcd for $C_{10}H_6S_2O_4$: C, 47.23; H, 2.38. Found: C, 46.91; H, 2.65.

Purification of Reagents. Reagent grade sodium sulfite, potassium cyanide, acetic acid, chloroacetic acid, dichloroacetic acid, trifluoroacetic acid, and sodium acetate were used without further purification. 1,4-Dioxane was purified by the procedure of Hess and Frahm,[25] and the freshly distilled dioxane was then frozen and stored at −20 °C to prevent the formation of peroxides prior to use. Doubly distilled water was used in all kinetic runs.

Procedure for Kinetic Runs. Reaction of Excess Sulfite or Cyanide with Substrates. In the runs using cyanide, 1:1 CN^-/HCN buffers were prepared by adding 1 mol of perchloric acid (as a dilute standardized solution in aqueous dioxane) to an aqueous dioxane solution containing 2 mol of cyanide. The resulting concentrated stock 1:1 buffer solution was then diluted further to achieve the cyanide concentration desired for a particular run.

The reactions of **1** and **4** were followed by stopped-flow spectrophotometry by mixing an equal volume of a 60% dioxane solution of either **1** or **4** with a solution of either sodium sulfite or 1:1 CN^-/HCN buffer in the same solvent. The reactions of **1** were followed at 296 nm and those with **4** at 304 nm.

Because of the rapid hydrolysis of **2** in aqueous dioxane, the stopped-flow procedure for following its reaction with sulfite involved mixing an equal volume of a solution of **2** in anhydrous dioxane with one of a solution of sodium sulfite in 20% dioxane. This procedure has been shown by Kice and Mullan[26] to be valid for following the kinetics of rapid nucleophilic substitution reactions of sulfinyl sulfones. The reaction was followed at 310 nm.

The much slower reactions of α-disulfones **3** and **6** were followed by conventional spectrophotometry. A known volume (3.6 mL) of either a solution of sodium sulfite or a 1:1 CN^-/HCN buffer in 60% dioxane was placed in a spectrophotometer cell in the thermostatted cell compartment of a Cary Model 17 spectrophotometer, and, once thermal equilibration was achieved, the reaction was initiated by injecting 36 μL of a 10^{-2} M solution of either **3** or **6** in anhydrous dioxane into the other solution with immediate mixing. The reactions involving **3** were followed at 313 nm and those involving **6** at 322 nm.

Regeneration of 1 from 7 and 8. Solutions of **7** (or **8**) were prepared by reacting **1** (10^{-4} M) with either 5×10^{-4} M CN^- (1:1 CN^-/HCN buffer) or 5×10^{-4} M sodium sulfite in 60% dioxane. To 3.6 mL of these solutions in a thermostatted spectrophotometer cell was then added 36 μL of a concentrated chloroacetic acid/sodium chloroacetate buffer (these buffers contained 1 M sodium chloroacetate and either 0.5, 1.0, or 2.0 M chloroacetic acid), and the increase in the absorbance of the solution with time at 296 nm was then followed. The final absorbance at 296 nm corresponded in each case to the complete regeneration of **1**, and the final complete spectrum in the ultraviolet region corresponded to that expected for a 10^{-4} M solution of **1**.

Regeneration of 4 from 9 and 10. To study the regeneration of **4** from **9** a solution of **9** was prepared by dissolving 1.1 mg of **4** and 12.6 mg of sodium sulfite in 25 mL of 60% dioxane. This solution was placed in one of the reservoir syringes of a stopped-flow spectrophotometer, while chloroacetate buffers of varying pH were placed in the other reservoir syringe. Upon mixing of the two solutions the change in the optical density of the solution with time at 304 nm was followed.

The procedure for following the regeneration of **4** from **10** was similar except that in this case a solution of an equilibrium mixture of **4** and **10** was prepared by dissolving 2.2 mg of **4** in 50 mL of a 1:1 CN^-/HCN buffer in 60% dioxane having $[CN^-] = 0.002$ M. This was then placed in one of the reservoir syringes of the stopped-flow spectrophotometer and mixed with different chloroacetate buffers.

Slow Further Reaction of 10 to Give 11. To 3.6 mL of a 60% dioxane solution containing $[CN^-] = [HCN] = 0.016$ M was added 36 μL of a 10^{-2} M solution of **4** in pure dioxane, and the absorbance of the solution at 368 nm (λ_{max} for **11**) was monitored periodically during the course of a week. At the end of that time the absorbance at 368 nm corresponded to only 0.27 of that expected for complete conversion of **10** to disulfide **11**. The solution was then treated with sufficient concentrated chloroacetic acid buffer to convert all of the cyanide ion to HCN (and allow any **10** still present to revert to **4**), and the complete spectrum of the solution was examined. While there was evidence for the regeneration of some **4**, the amount was modest; comparison with known spectra of **4**, **11**, and **12** suggested that a considerable amount of thiolsulfinate **12** was present.

Failure to Regenerate 3 or 6 on Acidification of Final Reaction Solutions from Reaction of 3 or 6 with Sulfite and Cyanide. The final reaction solutions from the reaction of **3** (10^{-4} M) with either 1×10^{-3} M cyanide ion in a 1:1 CN^-/HCN buffer or 5×10^{-3} M sulfite ion were acidified by the addition of 36 μL of a chloroacetate buffer containing 1 M $ClCH_2COO^-$ and 2 M $ClCH_2COOH$. The absorbance of the solution in the region around 313 nm, where **3** has its absorbance maximum, was then monitored with time. There was *no* increase in optical density at 313 nm; regeneration of **3** under these conditions therefore does not occur.

α-Disulfone **6** (10^{-4} M) was reacted at 25 °C with a 1:1 CN^-/HCN buffer containing $[CN^-] = 0.004$ M, and as soon as the rather rapid reaction was complete ($t = 3.5$ min for 10 half-lives) the 3.6 mL of reaction solution was acidified by the addition of 36 μL of 1:1 chloroacetate buffer, 1.0 M in chloroacetic acid. Acidification led to no increase with time in the optical density at 322 nm, as would have occurred if **6** had been regenerated. Instead, there was a slow further decrease in the absorbance at 322 nm ($k_1 = 5 \times 10^{-4}$ s^{-1}), presumably due to the slow hydrolysis (or decomposition) of the intermediate (**15**) that had been formed in the initial rapid reaction.

Preparation of Bunte Salt *S*-Oxide 16. A solution of 6.3 mg (0.05 mmol) of sodium sulfite in 1 mL of water was added quickly at room temperature with good stirring to a solution of 13.2 mg (0.05 mmol) of **2** in 1 mL of anhydrous dioxane. As soon as the addition was complete the clear solution was frozen, and the solvents were removed by lyophilization. The white crystalline residue of **16** so obtained was used without further purification. In the 900–1300-cm^{-1} region the infrared spectrum of **16** (KBr) showed a strong peak centered at 1220 cm^{-1}, a peak of moderate intensity at 1115 cm^{-1}, and a strong, broad band consisting of a series of overlapping absorptions between 940–1070 cm^{-1}. The ultraviolet spectrum (60% dioxane) had a λ_{max} at 280 nm (ϵ 6400). When heated slowly in a sealed capillary tube **16** began to decompose slowly above 40 °C with substantial contraction of the sample in volume and apparent evolution of a gas. The decomposition was rapid at 70 °C. Exposure of this gas to a solution of barium chloride caused the solution to become turbid, suggesting the gas is probably sulfur trioxide. The solid remaining after the decomposition of **16** did not melt below 300 °C.

Kinetics and Products of the Decomposition of Bunte Salt *S*-Oxide 16. A 1.2×10^{-4} M solution of **16** in 60% dioxane was prepared, and 3.6 mL of the solution was placed in a thermostatted, 1-cm spectrophotometer cell in the Cary 17. A 36-μL amount of 1 M $HClO_4$ solution was then added to this solution. One observed the immediate disappearance of the 280-nm peak associated with **16** and the appearance of the spectrum characteristic of cyclic thiolsulfonate **1** with peaks at 296 and 262 nm. Based on the optical density at 296 nm and the initial concentration of **16**, the yield of **1** under these conditions is essentially quantitative.

In a second similar experiment 3.6 mL of the 1.2×10^{-4} M solution of **16** was treated with 72 μL of a 1:1 acetate/acetic acid buffer ($[AcO^-] = [AcOH] = 1$ M). The disappearance of the peak for **16** at 280 nm was now relatively slow and could be followed by conventional spectrophotometry. A scan of the spectrum of the final solution at the end of the reaction showed no evidence of a peak at 296 nm. The ultraviolet spectrum of the final solution was very similar to that for disulfinate **17**. The final reaction solution was then acidified with sufficient concentrated perchloric acid to neutralize the buffer and give $[H^+] = 10^{-2}$ M, and the spectrum was then rescanned. The change in the spectrum was essentially the same as that observed[13] when a solution of **17** is acidified. Of particular importance, there was a small decrease in absorbance at 296 nm. Were **16** decomposing in the acetate buffer to yield some other species than **17** that was capable of yielding **1** readily upon acidification to pH 2, acidification of the final reaction solution would have led to the appearance of the 296-nm peak associated with **1**. One should also note that other work in this laboratory[2] has indicated that the reaction of a sulfenic acid with a sulfinic acid to give a thiolsulfonate will take place sufficiently readily in 60% dioxane in a 1:1 acetate buffer, so that if decomposition of **16** in that buffer led to **18** (presumably as its monoanion, given the pK_a's of the $-SO_2H$ and more weakly acidic $-SOH$ groups) it would go over to **1** in the buffer.

Additional kinetic experiments on the decomposition of **16** were carried out by adding varying amounts of the concentrated acetate buffer to 3.6 mL of the solution of **16** and following the change in absorbance with time at 280 nm.

In 1:1 chloroacetate buffers, the kinetics were followed in the same way as in acetate buffers. The behavior of **16** was slightly different than in acetate buffers in that the final reaction solution had a slight absorption peak at 296 nm, indicating some **1** had been formed. However, the fact that upon acidification with excess perchloric acid the absorbance of the final reaction solution again decreased at 296 nm shows that **17** is still the more important product.

In 1:1 dichloroacetate buffers the rate, although fast, was still slow enough to be followed by conventional spectrophotometry. However, since under these conditions, as in more acid solutions, the essentially exclusive organic product is **1**, the kinetics were studied by following the increase in optical density at 296 nm rather than the change at 280 nm.

The rate of decomposition of **16** in either 10^{-2} M $HClO_4$ or a 1:1 trifluoroacetate buffer was too fast to be followed by conventional spectrophotometry. Rates in these media were therefore measured by stopped-flow spectrophotometry by mixing a solution of **16** with the acidic solution and then following the change in absorbance at 296 nm.

Reaction of Cyanide Ion with Cyclic Sulfinyl Sulfones 2 and 5. When a solution of **2** (2×10^{-4} M) in pure dioxane was mixed in the stopped-flow spectrophotometer with an equal volume of a series of CN^-/HCN buffers in 20% dioxane, $[CN^-] = 0.002$–0.008 M, and the change in the absorbance with time at 310 nm (λ_{max} for **2**) was monitored, the following results were obtained. For $[CN^-] \geq 0.002$ M after mixing, plots of log $(A - A_\infty)$ vs. time were nicely linear, but the experimental first-order rate constant ($k_1 = 6.6$ s^{-1} for 1:1 CN^-/HCN buffer) was independent of $[CN^-]$. For $[CN^-] = 0.001$ M, plots of log $(A - A_\infty)$ vs. time showed some curvature; the initial slopes were about 75% those for the higher cyanide concentrations, while the slopes of the final portions of each run were about half those for the higher cyanide concentrations. Although independent of cyanide concentration, the rates for $[CN^-] \geq 0.002$ M were dependent on the CN^-/HCN buffer ratio, being approximately twice as large in a series of 2:1 CN^-/HCN buffers as they were in the series of 1:1 CN^-/HCN buffers. Obviously, what is being measured is not the rate of reaction of CN^- with **2** since this would show a first-order dependence on $[CN^-]$ throughout. On the other hand, the dependence of the rate on buffer ratio indicates that the process being measured is one whose rate depends on the concentration of $[OH^-]$. Since cyanide ion is reactive enough compared to hydroxide ion toward acyclic aromatic sulfinyl sulfones so that reaction with cyanide is the only process of kinetic importance in CN^-/HCN buffers,[26] it is hard to believe that what we are following here is the alkaline hydrolysis of **2** itself. Therefore we are inclined to believe that the explanation for the peculiar kinetic behavior observed with **2** and CN^- is that the opening of the sulfinyl sulfone ring in **2** by cyanide is more rapid at $[CN^-] \geq 0.002$ M than the process we are following but does not lead to much of a change in absorbance at 310 nm. Hydrolysis of the intermediate resulting from this reaction, presumably a sulfinyl cyanide, $-S(O)CN$, does involve a sizeable decrease in absorbance at 310 nm, and it is this process that is what one follows via stopped-flow studies. The rate of hydrolysis of the sulfinyl cyanide might be expected to depend on $[OH^-]$ but be independent of $[CN^-]$. Due to the rate of spontaneous hydrolysis of sulfinyl sulfones, all kinetic studies using stopped-flow spectrophotometry with these substrates in 60% dioxane have to be done by mixing a solution of the sulfinyl sulfone in anhydrous dioxane with a 20% dioxane solution of the nucleophilic reactant,[26] with a resultant period immediately after mixing where *small* changes in absorbance cannot be measured reliably. Because of this, it is not possible in the present system to ascertain whether or not there is a small, rapid initial absorbance change with the rate proportional to $[CN^-]$ preceding the process associated with the large absorbance change which is easy to measure. We tried to see if the situation could be improved by using a different wavelength to follow the reaction but without success.

In the case of the reaction of **5** with cyanide the situation is no better because here the total overall absorbance change associated with the transformation of **5** to the final reaction products is so small as to make any reliable kinetic studies impossible, given the special type of mixing that has to be employed in stopped-flow kinetic work with sulfinyl sulfones.

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Registry No.—**1**, 25331-82-2; **2**, 63059-28-9; **3**, 64728-07-0; **4**, 40227-43-8; **5**, 57821-65-5; **6**, 62609-77-2; **7**, 64754-26-3; **8**, 64754-27-4; **9**, 64754-28-5; **10**, 64754-29-6; **16**, 64754-25-2; sulfite, 14265-45-3; cyanide, 57-12-5.

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$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

the experimental first-order rate constant is equal to $(k_1 + k_{-1})$.[6]
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(10) A value of 5×10^{-5} s^{-1} for k_r in eq 5 would mean that K_{eq} for the **6** + $CN^- \rightleftarrows$ **15** equilibrium was only 600 times larger than K_{eq} for the **4** + $CN^- \rightleftarrows$ **10** equilibrium. However, there are good reasons to believe it should actually be at least 100 times larger than this and that k_r for **15** is therefore in actuality much smaller than 5×10^{-5} s^{-1}. Specifically, other studies[11] have suggested that the equilibrium constant for a ring-opening reaction involving a cyclic α-disulfone will normally be much larger than for the same reaction and the analogous cyclic sulfinyl sulfone. Since results to be discussed in the next section indicate that K_{eq} for a reaction involving **2** is 5×10^4 times larger than K_{eq} for the same reaction involving **1**, one would certainly expect K_{eq} for the **6** + $CN^- \rightleftarrows$ **15** equilibrium to be at least 10^4 larger than K_{eq} for the **4** + $CN^- \rightleftarrows$ **10** equilibrium, and therefore that k_r for **15** must be much smaller than 5×10^{-5} s^{-1}.
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(14) Since no sulfite is present initially, the reverse of step k_r cannot be important at the start of the decomposition of **16**. Were it to become significant during the later stages of the reaction, one would see this manifested in a decline in the rate of disappearance of **16** and upward curvature in the first-order rate plots. This was not observed. For the reverse of step k_r to be kinetically important it would have to be faster than k_{hyd}. Three factors combine to prevent this from being the case in the present system, despite the large rate constant ($k_2 = 3 \times 10^5$ M^{-1} s^{-1}) for the reaction of **2** with SO_3^{2-}. These are the following: (a) even at the end of the reaction the total amount of sulfite plus bisulfite present is only 10^{-4} M, i.e., equal to the initial concentration of **16**; (b) the fraction of sulfite remaining unprotonated in the acetate buffers is very small; (c) the rate of hydrolysis of **2** in the acetate buffers is quite fast ($k_{hyd} \geq 0.02$ s^{-1}).
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Diaziridinones (2,3-Diazacyclopropanones). Structure (X Ray).[1a] Thermal Decomposition via a Nitrenoid Fragment[1b]

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The structure of a diazacyclopropanone, bis(p-bromo-α,α-dimethylbenzyl)diaziridinone (**3**), has been determined by x-ray analysis. The substituents attached to the nitrogen atoms are 56° above and below the plane defined by the ring atoms; the bond lengths in the ring are 1.60 (N–N) and 1.325 Å (N–CO). Thermal decomposition of the diaziridinone affords the following (in moles of product per mole of reactant): p-bromo-α,α-dimethylbenzyl isocyanate (**9**) (0.35), p-bromo-N-(1-methylethylidene)benzenamine (**10**) (0.24), N-(1-p-bromophenylethylidene)methanamine (**11**) (<0.01), p-bromo-α-methylstyrene (**12**) (0.15), and p-bromocumene (**13**) (0.01). The major path of decomposition is fragmentation to the isocyanate **9** and a nitrenoid species which rearranges (aryl migration) to imine **10**.

Diaziridinones (2,3-diazacyclopropanones) pose several problems of interest in structure and reactivity.[2] NMR and IR data for N,N'-di-*tert*-alkyldiaziridinones are suggestive of the nonplanar trans structure **1**.[2a] Physical data and reactions of a bicyclic diaziridinone **2** are in accord with structure **2**, although the NMR shows a single methyl signal (and a single methylene signal) even down to −150 °C.[2c]

Here we report the structure of the diaziridinone **3**, determined by x-ray analysis, and a study of the thermal decomposition of this diaziridinone.

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