THE JOURNAL OF Organic Chemistry

VOLUME 47, NUMBER 17

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AUGUST 13, 1982

Reaction of Thiolate, Sulfite, and Cyanide Ions with Cyclic Aryl Thiolsulfinates: Dibenzo[*c*,*e*]-1,2-dithiin and Naphtho[1,8-*cd*]-1,2-dithiole 1-Oxides

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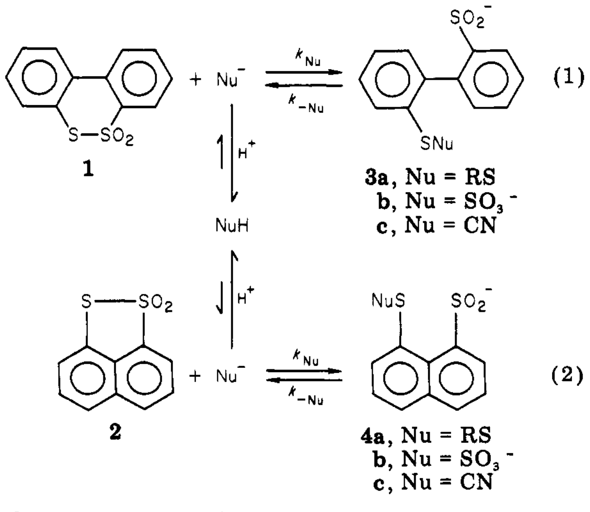
Received February 9, 1982

The behavior of cyclic thiolsulfinates **5** and **6** (dibenzo[*c*,*e*]-1,2-dithiin 1-oxide and naphtho[1,8-*cd*]-1,2-dithiole 1-oxide) upon treatment with either sulfite, cyanide, or *t*-BuS$^-$ ions has been examined and compared with the behavior of the corresponding thiolsulfonates **1** and **2** (dibenzo[*c*,*e*]-1,2-dithiin and naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxides). Very marked differences are observed. Whereas thiolsulfonates **1** and **2** are converted essentially quantitatively to ring-open substitution products (**3** and **4**) upon treatment with excess sulfite, cyanide, or *t*-BuS$^-$, with thiolsulfinates **5** and **6** the equilibrium constants for opening of the sulfur-containing ring are so much smaller that only in the case of **5** and *t*-BuS$^-$ is the equilibrium constant large enough that a significant fraction of the thiolsulfinate is converted to the ring-opened product (**7** or **8**) at equilibrium. Kinetic studies of the rates of nucleophile-catalyzed racemization of optically active **5** and **6** show that the major factor responsible for the dramatic difference in the magnitude of the equilibrium constants is not a decrease in the rate constant for opening of the ring by the nucleophile but rather a huge increase in the rate constant for the reverse of the ring-opening reaction, which in the case of the thiolsulfinates involves displacement of the nucleophile (Nu$^-$) from SNu by a sulfenate (SO$^-$) group, whereas for the thiolsulfonates it is a sulfinate (SO$_2^-$) group that performs the same displacement. In the **5**–*t*-BuS$^-$ system the rate constant for the displacement by the sulfenate is 30 000 times faster than the rate constant for the corresponding displacement in the **1**–*t*-BuS$^-$ system involving the sulfinate; this provides the first quantitative measure of just how much more reactive a sulfenate ion is as a nucleophile than the corresponding sulfinate. Other aspects of the kinetics of the reactions of **5** and **6** with these nucleophiles provide additional information on the behavior of **7** and **8** and their conjugate acids and thereby furnish new insight into the chemistry and reactivity and of arenesulfenates and arenesulfenic acids.

Upon treatment with excess thiolate, sulfite, or cyanide ion the thiolsulfonate ring in cyclic thiolsulfonates **1** and **2** is rapidly cleaved, and the thiolsulfonates are quantitatively converted to **3** and **4** (Nu = RS, SO$_3^-$, or CN) as shown in eq 1 and 2 (step k_{Nu}).[1,2] The reactions are analogous to the reactions[3] of open-chain aryl thiolsulfonates with the same reagents, i.e., Nu$^-$ + ArSSO$_2$Ar → ArSNu + ArSO$_2^-$.

If the final reaction solution is acidified with a carboxylic acid buffer sufficiently acidic to protonate RS$^-$, SO$_3^{2-}$, or CN$^-$ to RSH, HSO$_3^-$, or HCN, then **3** and **4** revert readily and quantitatively (step k_{-Nu}) to cyclic thiolsulfonates **1** and **2**, respectively.[1,2] By a suitable sequence of kinetic measurements one may obtain both k_{Nu} and k_{-Nu} for such systems, and from these the equilibrium constant, $K_{eq} = k_{Nu}/k_{-Nu}$, for each reaction.



1

3a, Nu = RS
b, Nu = SO$_3^-$
c, Nu = CN

2

4a, Nu = RS
b, Nu = SO$_3^-$
c, Nu = CN

Acyclic aryl thiolsulfinates, ArS(O)SAr, can also be cleaved by thiolate, sulfite, or cyanide ion, although at a rate about 20–40 times slower than that for corresponding thiolsulfonate, ArSO$_2$SAr.[4] The cleavage takes place by

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[1] Chau, M. M.; Kice J. L. *J. Org. Chem.* **1978**, *43*, 914.

[2] Boduszek, B.; Kice, J. L. *J. Org. Chem.* **1982**, *47*, 2055.

[3] Kice, J. L.; Rogers, T. E.; Warheit, A. C. *J. Am. Chem. Soc.* **1974**, *96*, 8020.

[4] Kice, J. L.; Liu, A. C-C. *J. Org. Chem.* **1979**, *44*, 1918.

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Table I. Kinetics of Reaction of Dibenzo[*c*,*e*]1,2-dithiin 1-Oxide (5)[a] with 2-Methyl-2-propanethiolate at 25 °C in 60% Dioxane

$10^4[RS^-]$, M	$10^4[RSH]$, M	k_1, s^{-1} [b]	k_2, s^{-1}
13.0	17.0	54.1	
	32.0	56.7	
11.3	45.0	46.2	0.0083
9.0	11.0	39.8	
8.0	12.0	33.9	
	22.0	34.4	
7.5	30.0	33.8	0.0082
6.5	8.5	27.7	
4.0	6.0	17.1	
3.0	7.0	15.4	
	12.0	17.3	
1.5	3.5	11.1	
2.84[c]	37.2[c]	15.4	
2.13[c]	27.9[c]	12.2	
1.42[c]	18.6[c]	9.7	
0.71[c]	9.3[c]	7.3	

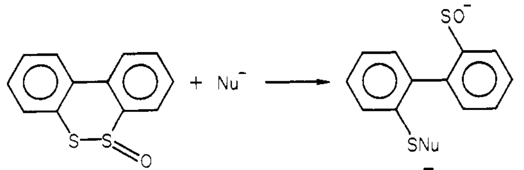
[a] $[5]_0 = 5.0 \times 10^{-5}$ M. [b] Rates reproducible to ±5%. [c] Runs carried out in a borate buffer (pH 12.60) in which *t*-BuSH (pK_a = 13.72 in 60% dioxane) will be 7.1% ionized to *t*-BuS⁻.

attack of the nucleophile on the dicoordinate sulfur of the thiolsulfinate (eq 3a). The arenesulfenate ($ArSO^-$) liberated can then be converted to a second mole of ArSNu in the manner outlined in eq 3b.[4]

$$Nu^- + ArS(O)SAr \rightarrow ArSO^- + ArSNu \qquad (3a)$$

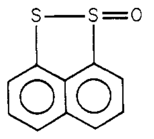
$$ArSO^- \underset{}{\overset{H^+}{\rightleftharpoons}} ArSOH \xrightarrow[H^+]{Nu^-} ArSNu + H_2O \qquad (3b)$$

The behavior of ArSS(O)Ar with such nucleophiles suggests that cyclic aryl thiosulfinates such as dibenzo[*c*,*e*]-1,2-dithiin 1-oxide (**5**) and naphtho[1,8-*cd*]-1,2-dithiole 1-oxide (**6**) should be capable of being cleaved by RS^-, SO_3^{2-}, or CN^- in the manner shown for **5** in eq 4.



(4)

5 **7**



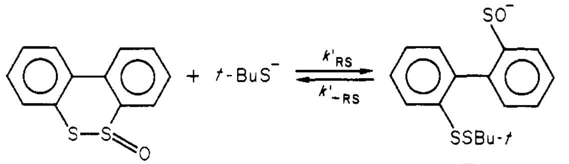
6

However, the sulfenate ion (SO^-) in **7** will differ markedly from the sulfinate ion (SO_2^-) in **3** in four important respects: (a) it is the conjugate base of a considerably weaker acid; (b) it is a much more reactive nucleophile;[5] (c) its conjugate acid (SOH) can react further with a second Nu^- in the manner shown in eq 3b; (d) neither it nor its conjugate acid are stable, one mode of decomposition being disproportionation to SO_2^- and S^-.[6] These considerations suggested that the reactions of **5** or **6** with nucleophiles like RS^-, SO_3^{2-}, or CN^- might well exhibit very different behavior from what is observed for the reactions **1** and **2** with the same nucleophiles.

In the present study we have examined the reactions of **5** and **6** with *t*-BuS⁻, SO_3^{2-}, and CN^- and find that these do indeed exhibit quite different behavior than the reactions of these same nucleophiles with **1** and **2**. The differences can in each case be attributed to one or more of the differences between a sulfenate (SO^-) and a sulfinate (SO_2^-) alluded to above. For this reason detailed study of the kinetics of these reactions provides several interesting new insights into the chemistry and reactivity of arenesulfenates and arenesulfenic acids.

Results and Discussion

Reaction of 2-Methyl-2-propanethiolate (*t*-BuS⁻) with 5. In 60% dioxane (v/v) treatment of **5** with *t*-BuS⁻ and *t*-BuSH results in a very rapid increase in the absorbance of the solution at 300 nm the rate of which is dependent on [*t*-BuS⁻]. This is followed by a considerably slower decrease in the absorbance at 300 nm the rate of which is *independent* of the concentration of either thiol or thiolate. The very rapid first reaction is the opening of the thiosulfinate ring in **5** by *t*-BuS⁻ to give **7a** (eq 5).



(5)

5 **7a**

The slower thiol-independent second stage is the decomposition of sulfenate **7a**. The rates of both processes can be followed by stopped-flow spectrophotometry. The experimental first-order rate constants, k_1, for the first stage for the various runs are shown in Table I. The rate constant for the second stage, k_2, was determined in only a very limited number of runs. These data are also given in Table I.

At the lower thiolate concentrations ($A_\infty - A_0$) for the first stage increases with [*t*-BuS⁻] in a manner that indicates that the equilibrium constant for the reaction of *t*-BuS⁻ with **5** to give **7a** is such that unless [*t*-BuS⁻] ≥ 10^{-3} M the conversion of **5** to **7a** is not complete at equilibrium. For this reason k_1 as measured is equal to

$$k_1 = k'_{-RS} + k'_{RS}[t\text{-BuS}^-]$$

where k'_{RS} and k'_{-RS} are the rate constants for the forward and reverse steps of the equilibrium in eq 5. A plot of k_1 vs. [*t*-BuS⁻] gives k'_{RS} as the slope and k'_{-RS} as the intercept.[7] The values so obtained are $k'_{RS} = 3.8 \times 10^4\ M^{-1}\ s^{-1}$ and $k'_{-RS} = 4.5\ s^{-1}$, and from these $K'_{eq} = (k'_{RS}/k'_{-RS}) = 8.4 \times 10^3\ M^{-1}$. The fact that k'_{-RS} as obtained from a plot of k_1 vs. [*t*-BuS⁻] for the runs in a borate buffer of pH 12.60 is the same as k'_{-RS} as estimated from the data for runs which were carried out in *t*-BuS⁻-*t*-BuSH solutions of higher pH (13.1 to 13.6) indicates that the sulfenate group of **7a** is not protonated to any large extent to SOH in the borate buffer and that the pK_a of the conjugate acid of **7a** in 60% dioxane must be less than 12.3. Were a significant fraction of **7a** present in the SOH (sulfenic acid) form in the borate buffer, the plot of the data for that buffer would give a proprotionately smaller apparent value

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(5) Kice, J. L.; Rogers, T. E. *J. Am. Chem. Soc.* **1974**, *96*, 8009.

(6) (a) Vinkler, E.; Klivenyi, F.; Lazar, J.; Kozakiewicz, I. *Acta Chim. Acad. Sci. Hung.* **1969**, *60*, 167. (b) Vinkler, E.; Klivenyi, F. *Int. J. Sulfur Chem.* **1973**, *8*, 111.

(7) The most accurate value for k'_{-RS} is obtained from a plot of the rate data for the last four runs in Table I where the reaction was carried out in the presence of 0.001–0.004 M *t*-BuSH in a borate buffer in which the thiol is 7.1% ionized. However, the data for the remaining runs, where [*t*-BuS⁻] is generally much higher (4×10^{-4}–13×10^{-4} M), also give a plot with the same value of k'_{-RS} within experimental error.

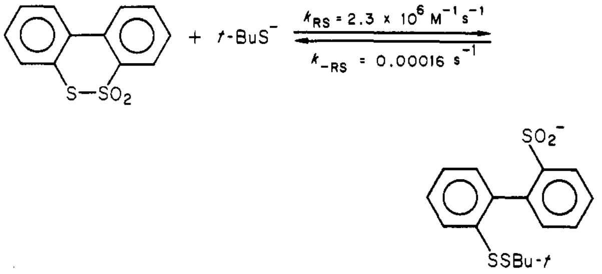
Table II. Racemization of Optically Active 5 and 6 in the Presence of 2-Methyl-2-propanethiol (0.01 M) in Acetate Buffers at 25 °C in 60% Dioxane

thiolsulfinate (concn, M)	buffer	pH[a]	$10^4 k_\alpha$, s^{-1} [b]
(−)-**5**	$[AcO^-] = [AcOH] = 0.02$ M	7.44	1.4
(0.05)	$[AcO^-] = 2[AcOH] = 0.02$ M	7.74	3.0
(+)-**6**	$[AcO^-] = [AcOH] = 0.02$ M	7.44	3.5
(0.05)	$[AcO^-] = 2[AcOH] = 0.02$ M	7.74	6.9

[a] Assuming pK_a for HOAc in 60% dioxane is 7.44.[9]
[b] Rates reproducible to ±10%.

of k'_{-RS} than that estimated from the data for the runs at higher pH.

Comparison of k'_{RS}, k'_{-RS}, and K'_{eq} for the reaction of thiosulfinate **5** with t-BuS$^-$ with the corresponding rate and equilibrium constants for the reaction of the same thiolate with thiolsulfonate **1**[2] (eq 6) is most informative. The value



(6)

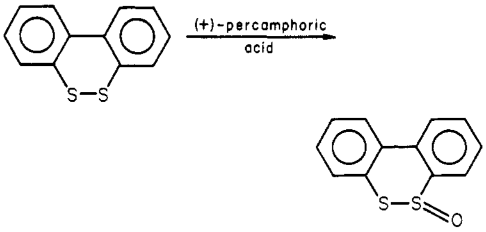
of k'_{RS}/k_{RS} (0.017) is in line with previous findings[4] regarding the relative reactivity of PhSS(O)Ph vs. PhSSO$_2$Ph toward nucleophiles. The ratio k'_{-RS}/k_{-RS}, which has a value of 3×10^4, is of particular interest because it provides for the first time a quantitative measure of just how much more reactive as a nucleophile a sulfenate is than the corresponding sulfinate.

Because k'_{-RS} is 30000 times larger than k_{-RS}, while k'_{RS} is about 60 times smaller than k_{RS}, the equilibrium constant for eq 5 is slightly over 10^6 *smaller* than that for eq 6 ($K'_{eq}/K_{eq} = 6 \times 10^{-7}$). On a free-energy basis the opening of the thiolsulfinate ring in **5** by t-BuS$^-$ is 8.5 kcal/mol less favorable than the opening of the thiolsulfonate ring in **1** by the same reagent.

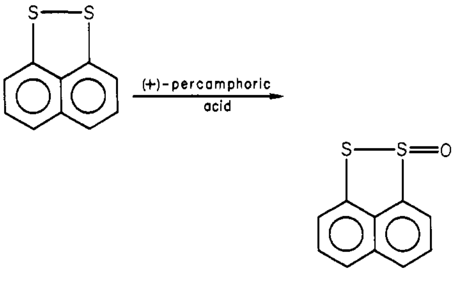
The fact that K'_{eq}/K_{eq} is only 6×10^{-7} suggests that in the case of nucleophiles like SO_3^{2-} or CN$^-$, where K_{eq} for the reaction of the nucleophile with **1** is from 10^4 to 10^5 times smaller than K_{eq} for the reaction of t-BuS$^-$ with **1**, one is likely to find that K'_{eq} for the reaction of **5** with such nucleophiles will be so small that, even at quite high nucleophile concentrations, no significant fraction of the thiolsulfinate will be converted to **7** at equilibrium. Since the equilibrium constants for the reaction of the five-membered cyclic thiolsulfonate **2** with nucleophiles are generally about 20 times smaller than those for **1**,[1,2] the extent of ring opening at equilibrium in the reaction of **6** with such nucleophiles should be even smaller than for **5**.

In cyclic thiolsulfinate–nucleophile systems exhibiting such behavior there is, however, a way, thanks to the chiral nature of the sulfinyl group in **5** and **6**, whereby one can measure k'_{Nu} for the reaction of a nucleophile with **5** (or **6**) even though the fraction of the thiolsulfinate that will be present in the ring-opened form at equilibrium is too small to be measurable.

Partially optically active (−)-**5** and (+)-**6** can be prepared by asymmetric oxidation of the appropriate cyclic disulfides with (+)-percamphoric acid (eq 7 and 8), just as partially optically active (+)-PhS(O)SPh has been prepared[8] from PhSSPh by oxidation with the same reagent.

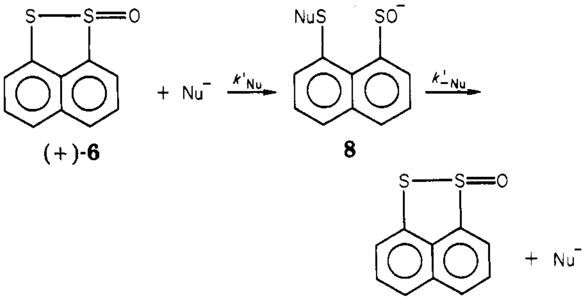


(−)-**5**; $[\alpha]_{436}$ −9.3° (60% dioxane) (7)



(+)-**6**; $[\alpha]_{546}$ +8.2° (60% dioxane) (8)

Reaction of a nucleophile with one of these optically active thiolsulfinates to open the ring gives an achiral species (**7** or **8**), and so reversion (step k'_{-Nu}) of **7** (or **8**) to **5** (or **6**) will give racemic thiolsulfinate (eq 9). The rate of racemization of the optically active thiolsulfinate (k_α) in the presence of the nucleophile should therefore be equal to $k'_{Nu}[Nu^-]$, and one should be able to obtain k'_{Nu}, even for systems where K'_{eq} is extremely small, from measurements of the rate of nucleophile-catalyzed racemization of optically active **5** or **6**.



(+)-**6** **8** (±)-**6** (9)

One can test whether one can in fact hope to obtain reasonably reliable values of k'_{Nu} by this procedure by examining the behavior of (−)-**5** plus t-BuSH in acetate buffers and comparing the value of k'_{RS} as estimated from k_α (eq 10) with the one measured directly (vide supra) in

$$k'_{RS} = \frac{k_\alpha}{C_{t\text{-BuSH}}} \times \frac{[AcOH]}{[AcO^-]} \times \frac{K_a^{HOAc}}{K_a^{t\text{-BuSH}}} \qquad (10)$$

much more basic media from the reaction of t-BuS$^-$ at much higher concentration with **5**. In acetate buffers of varying pH one finds that (−)-**5** does indeed undergo racemization in the presence of t-BuSH and that the rate of this racemization (k_α) is dependent on the concentration of added thiol $C_{t\text{-BuSH}}$ and on the buffer ratio $[AcO^-]/[AcOH]$, this latter fact showing that despite its extremely low concentration relative to t-BuSH, it is t-BuS$^-$ and *not* t-BuSH which is responsible for the nucleophile-catalyzed racemization. Relevant kinetic data for this system and also for the t-BuS$^-$-catalyzed racemization of (+)-**6** under the same conditions are given in Table II. On the assumption that the pK_a of acetic acid in 60% dioxane is

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(8) (a) Savige, W. E.; Fava, A. *Chem. Commun.* **1965**, 417. (b) Kice, J. L.; Large, G. B. *Tetrahedron Lett.* **1965**, 3537.

Table III. Nucleophile-Catalyzed Racemization of Optically Active 5 and 6 by Cyanide and Sulfite Ions at 25 °C in 60% Dioxane

thiolsulfinate (concn, M)	nucleophile	$10^4 \times$ [Nu$^-$], M	$10^4 \times$ [NuH], M	$10^3 k_\alpha$, s^{-1} [a]	k_α/[Nu$^-$], M^{-1} s^{-1}
(+)-**6** (0.04)	SO_3^{2-}	1.0	1.0	2.8	28
		1.5	1.0	4.5	30
		2.0	1.0	6.2	31
		2.0	2.0	5.7	29
		2.0	3.0	6.6	33
(−)-**5** (0.02)	SO_3^{2-}	5.0	5.0	4.1	8.2
		7.5	5.0	8.1	10.2
		10.0	5.0	9.9	9.9
(+)-**6** (0.05)	CN^-	1.0	1.0	7.0	70
		1.5	1.5	10.6	70
		2.0	2.0	15	75
		2.5	2.5	18	72
(−)-**5** (0.02)	CN^-	3.0	3.0	4.5	15
		5.0	5.0	7.0	14

[a] Rates reproducible to ±10%.

7.44[9] and that of *t*-BuSH is 13.72,[2] the measured k_α's in Table II give calculated values for k'_{RS} for **5** of 2.7×10^4 and 2.9×10^4 M^{-1} s^{-1} for the pH 7.44 and 7.74 runs, respectively. One sees that the value for k'_{RS} as estimated from k_α is slightly smaller than k'_{RS} as measured directly. Since there is probably at least ±0.1 pK unit uncertainty in pK(HOAc) − pK(*t*-BuSH), this could well be the origin of most of the difference. (On the other hand, since step k'_{-RS} is rapid, it could also be that reversion of **7a** to **5** leads to **5** with some net retention of configuration.) In any event the values of k'_{RS} as estimated from the two different types of measurements are close enough to suggest that in those systems where K'_{eq} is too small for k'_{Nu} to be able to be measured directly one should be able to use measurements of k_α for the Nu$^-$-catalyzed racemization of(−)-**5** or (+)-**6** to obtain a reasonably good estimate of k'_{Nu}.

The data for the racemization of (+)-**6** in Table II give a value for k'_{RS} for the reaction of that thiolsulfinate with *t*-BuS$^-$ of 6.7×10^4 M^{-1} s^{-1}.

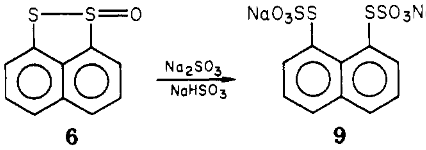
Reaction of Sulfite with 5 and 6. In sulfite–bisulfite buffers in 60% dioxane optically active (+)-**6** racemizes rapidly. The kinetic data, which are given in the first section of Table III, indicate that k_α is dependent on [SO_3^{2-}] and independent of [HSO_3^-] and that k_α/[SO_3^{2-}] = 30 M^{-1} s^{-1}. As discussed above, we believe that k_α/[SO_3^{2-}] should provide a reasonably good estimate of k'_{SO_3}, the rate of attack of sulfite ion on **6** to form **8b** (eq 9, Nu$^-$ = SO_3^{2-}). A further indication that this is correct is the following. The relative reactivity of sulfite vs. *t*-BuS$^-$ toward cyclic thiosulfonate **2** (k_{SO_3}/k_{RS}) is 7×10^{-4}.[1,2] A roughly similar value might be expected for k'_{SO_3}/k'_{RS} for the reaction of these two nucleophiles with **6**. The fact that a value for k'_{SO_3} of 30 M^{-1} s^{-1} results in k'_{SO_3}/k'_{RS} for **6** being 5×10^{-4} certainly suggests that taking $k'_{SO_3} = k_\alpha/[SO_3^{2-}]$ provides a satisfactory estimate for this rate constant.

Table IV. Rate of Disappearance of Thiolsulfinates 5 and 6 in Sulfite–Bisulfite Buffers in 60% Dioxane at 25 °C

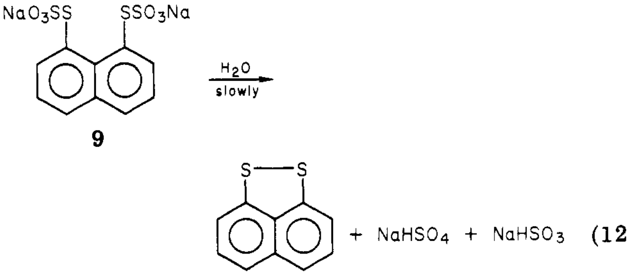
thiolsulfinate (concn, M)	[HSO_3^-], M	[SO_3^{2-}], M	[HSO_3^-]/[SO_3^{2-}]	$10^3 k_1$, s^{-1} [c]
6 (1×10^{-4})	0.010	0.030	0.33	1.04 [a]
		0.021	0.48	1.01
		0.0166	0.60	1.09
	0.015	0.025	0.60	2.87
	0.010	0.012	0.83	1.18
	0.0043	0.0043	1.0	0.24
	0.020	0.020	1.0	5.06
	0.018	0.012	1.5	3.65
	0.019	0.011	1.75	4.90
	0.020	0.010	2.0	5.46
	0.0225	0.0075	3.0	6.19
5 (9×10^{-5})	0.0025	0.0075	0.33	1.53 [a]
		0.0050	0.50	1.12
	0.0050	0.010	0.50	4.86
	0.0025	0.0025	1.0	0.54
	0.0050	0.0050	1.0	2.64 [b]
	0.0075	0.0075	1.0	6.62
	0.0050	0.0025	2.0	1.28
	0.010	0.0050	2.0	6.90
	0.0075	0.0025	3.0	2.74 [a]

[a] Average of two runs. [b] Average of four runs. [c] Rates reproducible to ±5%.

Treatment of **6** (1×10^{-4} M) with a solution containing both 0.01 M sulfite and bisulfite does not lead to any rapid change in the optical density of the solution, despite the fact that $k'_{SO_3}[SO_3^{2-}]$ under such conditions is presumably equal to 0.3 s^{-1}. Instead there is only a relatively slow change in the optical density ($k_{exp} = 1 \times 10^{-3}$ s^{-1}), and acidification of the reaction solution after this change is completed by the addition of excess chloroacetic acid buffer does not result in the regeneration of any detectable amount of **6**. The product of the reaction of **6** with sulfite under these conditions was shown in a separate experiment to be the di-Bunte salt **9** (eq 11). On being allowed to stand in solution, particularly an acid solution, this Bunte salt slowly breaks down (eq 12) to give naphtho[1,8-*cd*]-1,2-dithiole (**10**).



6 **9** (11)



9

10 (12)

The conversion of **6** to **9** in sulfide–bisulfite buffers can be conveniently followed by monitoring the increase in the optical density of the solution with time at 343 nm. Plots of log ($A_\infty - A$) vs. time show excellent linearity, indicating that the reaction is first order in thiosulfinate. The experimental first-order rate constants, k_1, for the disappearance of **6** at various sulfite and bisulfite concentrations are tabulated in the first section of Table IV.

From examination of Table IV it is immediately apparent that the dependence of k_1 on sulfite concentration is *not* a simple first-order dependence on [SO_3^{2-}]. Rather the kinetic data indicate that k_1 depends on sulfite and bisulfite in the manner shown in eq 13, with k_a = 1.0 M^{-2}

$$k_1 = k_a[SO_3^{2-}][HSO_3^-] + k_b[HSO_3^-]^2 \qquad (13)$$

s^{-1} and k_b = 12 M^{-2} s^{-1}. Since a rate term in [HSO_3^-] is kinetically indistinguishable from one in [H^+][SO_3^{2-}], the dependence of k_1 on [SO_3^{2-}] and [HSO_3^-] shown in eq 13 is explicable in terms of the mechanism shown in Scheme I. Such a mechanism will lead to the type of dependence of k_1 on [SO_3^{2-}] and [HSO_3^-] observed experimentally with

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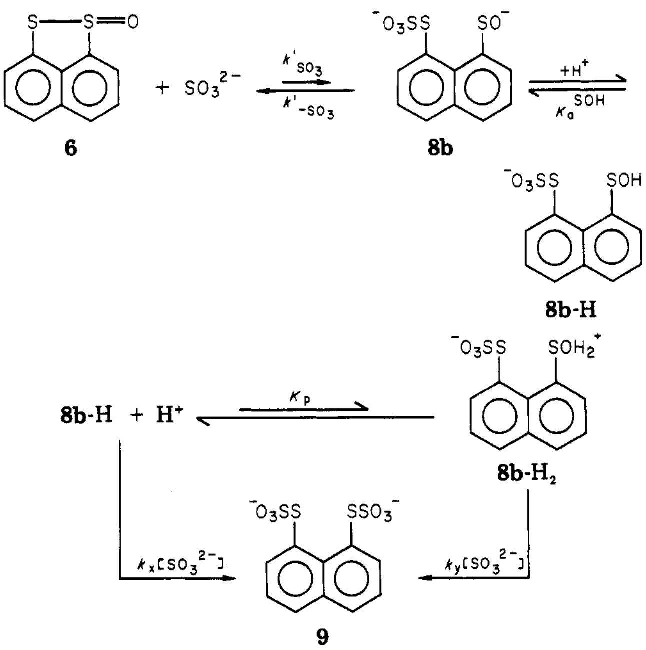
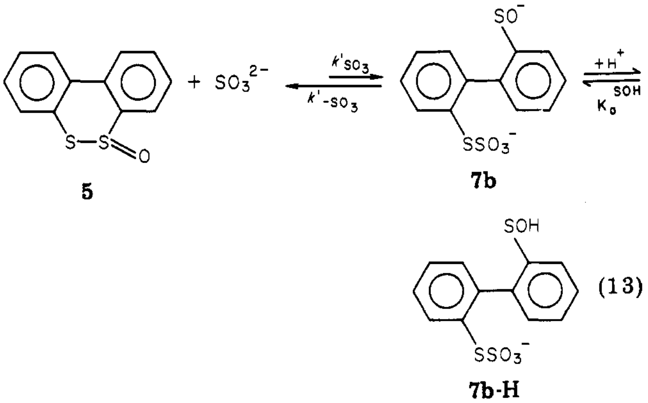
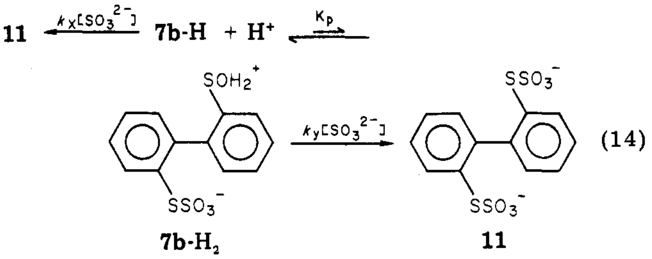
[9] Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolytic Solutions"; Reinhold: New York, 1950; p 581.

Scheme I. Mechanism of Reaction of 6 with Sulfite





(13)



(14)

$k_a = k_x(k'_{SO_3}/k'_{-SO_3})(K_2/K_a^{SOH})$ and $k_b = k_yK_pK_2(k'_{SO_3}/k'_{-SO_3})(K_2/K_a^{SOH})$, where K_2 is the second ionization constant for sulfurous acid ($HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$), and the other rate and equilibrium constants are as shown in Scheme I. In this scheme it is understood that, although the initial equilibria involving **6**, **8b**, and **8b**-H are rapidly established ($k'_{SO_3} = 30$ M^{-1} s^{-1}), the equilibrium constant for the **6** + $SO_3^{2-} \rightleftarrows$ **8b** step, i.e., k'_{SO_3}/k'_{-SO_3}, is so small that no significant fraction of the thiosulfinate is present at equilibrium as either **8b** or **8b**-H in the sulfite buffers, despite the relatively high (0.005–0.03 M) sulfite concentrations used.

The reaction of **5** with sulfite shows generally similar behavior. Optically active (–)-**5** undergoes rapid SO_3^{2-}-catalyzed racemization in sulfite–bisulfite buffers in 60% dioxane (second section of Table III); $k_\alpha/[SO_3^{2-}]$ is a constant and is equal to 10 M^{-1} s^{-1}. Such a value for k'_{SO_3} for **5** is consistent with expectations, based both on the reactivity of **5** vs. **6** toward *t*-BuS⁻ and on the relative reactivity of the six- (**1**) vs. the five-membered (**2**) cyclic thiolsulfonate toward nucleophiles,[1,2] that k'_{SO_3} will be significantly smaller for **5** than for **6**. While the rate of racemization of (–)-**5** in the presence of sulfite is rapid, the rate of disappearance of **5** in sulfite–bisulfite buffers is considerably slower, and the experimental first-order rate constants, k_1, for the disappearance of **5** at various sulfite and bisulfite concentrations (which are shown in the second part of Table IV) reveal that k_1 once again depends on sulfite and bisulfite concentration in the manner shown in eq 13. In the case of **5** both k_b (40 M^{-2} s^{-1}) and especially k_a (69 M^{-2} s^{-1}) are larger than the corresponding rate constants for **6**. The mechanism for the reaction of **5** with sulfite is therefore presumably analogous to that shown for **6** in Scheme I, i.e., a rapidly established equilibrium involving **5**, **7b**, and **7b**-H (eq 13), with an equilibrium constant such that only a very small fraction of **5** is present at equilibrium as either **7b** or **7b**-H, followed by rate-determining reaction of either **7b**-H or **7b**-H$_2$ with SO_3^{2-} (eq 14).

For cyclic thiolsulfonates **1** and **2** and sulfite (eq 1 and 2, Nu⁻ = SO_3^{2-}) the equilibrium constant for the reaction is 20 times larger for **1** than for **2**.[1] It therefore seems likely that k'_{SO_3}/k'_{-SO_3} for **5** will be considerably larger than k'_{SO_3}/k'_{-SO_3} for **6**. We think that it is this factor which is primarily responsible for k_a for **5** being so much larger than k_a for **6**. On the basis of the difference in pK_a's between the conjugate acids of **4b** and **3b**,[1] there is also reason to feel that the pK_a^{SOH} of **8b**-H will probably be 0.2–0.3 pK unit larger than the pK_a^{SOH} of **7b**-H. Such a difference in pK_a's would further contribute to making k_a for **5** larger than k_a for **6**. Taken together these two factors could, in our opinion, easily be responsible for most of the 70-fold difference between k_a for **5** and k_a for **6**. Such an interpretation leads to the conclusion that the rate constant for further reaction of the sulfenic acid with sulfite, k_x, is only slightly smaller for **8b**-H than for **7b**-H.

For the mechanism in Scheme I $k_b/k_a = k_yK_pK_2/k_x$. The fact that k_b^5/k_b^6 is only 3.3 while $k_a^5/k_a^6 = 70$ would therefore seem to indicate that k_yK_p for **7b**-H is considerably smaller than k_yK_p for **8b**-H. While one might anticipate that K_p could be somewhat larger for **8b**-H than for **7b**-H because of the close proximity and possible attractive interaction in **8b**-H$_2$ of the negatively charged SO_3^- group with the positively charged SOH_2^+ group, we would not have expected that the effect would be as large as a factor of 20. At the same time, however, we cannot see any obvious reason why k_y^5/k_y^6 should be significantly different in magnitude from k_x^5/k_x^6. Thus the origin of the marked difference in k_b^5/k_b^6 and k_a^5/k_a^6 is not entirely clear at this time.

It seems reasonable to believe that (k'_{SO_3}/k'_{-SO_3}) for **5** will probably be smaller than (k_{SO_3}/k_{-SO_3}) for **1** by about the same factor 6×10^{-7} as k'_{RS}/k'_{-RS} for **5** is smaller than k_{RS}/k_{RS} for **1**. Since k_{SO_3}/k_{-SO_3} for **1** is 1.7×10^5 M^{-1},[1] this means that k'_{SO_3}/k'_{-SO_3} for **5** is probably about 0.1 M^{-1}. While the magnitude of K_2/K_a^{SOH} is not known, we can, since we know from the racemization studies that equilibrium between **5** and **7b** plus **7b**-H will be established very rapidly, draw conclusions about its magnitude from the following experimental observation. Addition of 0.015 M SO_3^{2-} and HSO_3^- to a 10^{-4} M solution of **5** does not result in any detectable (≥4%) rapid initial change in the optical density of the solution prior to the slower change associated with the disappearance of **5** to form **11**. This means that the equilibrium ratio ([**7b**] + [**7b**-H])/[**5**] under these conditions is apparently ≤0.04. Since ([**7b**] + [**7b**-H])/[**5**] is equal to $(k'_{SO_3}/k'_{-SO_3})[SO_3^{2-}](1 + (K_2[HSO_3^-]/K_a^{SOH}[SO_3^{2-}]))$, if k'_{SO_3}/k'_{-SO_3} is ~0.1 M^{-1} and $[SO_3^{2-}]$ =

Table V. Rate of Disappearance of Thiolsulfinates 5 and 6 in Cyanide Buffers in 60% Dioxane at 25 °C

thiolsulfinate (concn, M)	buffer ratio, CN^-/HCN	$10^2[CN^-]$, M	$10^2[HCN]$, M	10^3k_1, s^{-1} [d]	k_2, M^{-1} s^{-1} [d]
6 (1×10^{-4})	10.0	1.25	0.125	*a*	8.2
		2.5	0.25	*a*	9.2
		5.0	0.50	*a*	7.9
	4.0	1.25	0.313	*a*	3.6
		2.5	0.625	*a*	3.9
		5.0	1.25	*a*	3.1
	2.0	1.25	0.625	*a*	1.8
		2.5	1.25	*a*	1.8
6 (1.5×10^{-4})	2.0	2.5	1.25	*a*	1.8
6 (1×10^{-4})	2.0	5.0	2.5	*a*	1.7
	1.0	1.25	1.25	*a*	0.88
		2.5	2.5	*a*	0.85
		5.0	5.0	(0.11) [c]	*b*
5 (0.9×10^{-4})	4.0	0.20	0.050	2.4	*b*
		0.40	0.10	2.6	*b*
		0.60	0.15	2.6	*b*
	2.0	0.20	0.10	1.1	*b*
		0.40	0.20	1.3	*b*
		0.80	0.40	1.5	*b*
	1.0	0.20	0.20	0.60	*b*
	0.40	0.40	0.40	0.75	*b*
		0.60	0.60	0.88	*b*
		1.0	1.0	1.3	*b*

[a] Plot of log $(A_\infty - A)$ vs. time (first-order plot) not linear. [b] Plot of $(A_\infty - A_0)/(A_\infty - A)$ vs. time (second-order plot) not linear. [c] Plot of log $(A_\infty - A)$ vs. time shows some upward curvature; the rate constant is the initial slope. [d] Rates reproducible to ±10%.

0.015 M, then $K_2/K_a^{SOH} \leq 25$, because if K_2/K_a^{SOH} had a significantly higher value than this, then one should see a measurable degree of rapid initial conversion of **5** to **7b** plus **7b**-H prior to the slower irreversible disappearance of **5** to form **11**. Since K_a for **5** is 69 M^{-2} s^{-1}, if $k'_{SO_3}/k'_{-SO_3} \simeq 0.1$ and $K_2/K_a^{SOH} \leq 25$, then $k_x \geq 26$ M^{-1} s^{-1}. This indicates that sulfenic acid **7b**-H is apparently somewhat more reactive toward sulfite ion than is thiolsulfinate **5**, a most intriguing observation when one considers that the reaction of **7b**-H with sulfite to form **11** is formally a displacement of OH^- by SO_3^{2-}, while the reaction of **5** is a displacement of the considerably lower pK_a sulfenate ion (SO^-).

Reaction of Cyanide with 5 and 6. In 1:1 CN^-–HCN buffers in 60% dioxane both (−)-**5** and (+)-**6** undergo rapid CN^--catalyzed racemization. The kinetics (second section of Table III) show that the rate of racemization (k_α) is proportional to $[CN^-]$ and that the values for $k_\alpha/[CN^-]$ for (+)-**6** (72 M^{-1} s^{-1}) and (−)-**5** (15 M^{-1} s^{-1}) are about twofold larger in each case than $k_\alpha/[SO_3^{2-}]$ for the corresponding SO_3^{2-}-catalyzed racemization.

In reaction with cyclic thiosulfonates **1** and **2** the reactivity of cyanide (k_{CN}) is about twice as great as that of sulfite (k_{SO_3}).[1] Toward the acyclic thiolsulfinate PhS(O)SPh the reactivity of cyanide is about half that of sulfite.[4] These two facts suggest that k'_{CN} for the reaction of cyanide with cyclic thiolsulfinates **5** and **6** should definitely by comparable to k'_{SO_3} for the reaction of sulfite ion with the same substrates. It is therefore reasonable to feel that the values of $k_\alpha/[CN^-]$ for **5** and **6** in Table III provide reliable estimates of k'_{CN} for each of these two thiolsulfinates, in the same way that the values of $k_\alpha/[SO_3^{2-}]$ have provided k'_{SO_3}.

Although k'_{CN} for both **5** and **6** is somewhat larger than k'_{SO_3}, just as $k_{CN} > k_{SO_3}$ for the two cyclic thiosulfonates **1** and **2**, one should also remember that for **1** and **2** K_{eq} for reaction with cyanide is only $\sim 0.07K_{eq}$ for reaction with sulfite, since $k_{-CN} \gg k_{-SO_3}$.[1] It would therefore not be surprising if k'_{CN}/k'_{-CN} for either **5** or **6** was significantly smaller than k'_{SO_3}/k'_{-SO_3} and if for a given cyanide concentration, there was significantly less **7c** (Nu = CN) or **8c** present at equilibrium than there was **7b** or **8b** for the same concentration of sulfite ion. In addition, since the pK_a of HCN is probably ~2.5 p*K* units larger than pK_2 for H_2SO_3,[10] the fraction of the sulfenate present in the sulfenic acid form (**7c**-H or **8c**-H) in a 1:1 CN^-–HCN buffer will be up to several hundred times smaller than the fraction of the sulfenate present in the sulfenic acid form (**7b**-H or **8b**-H in a 1:1 SO_3^{2-}–HSO_3^- buffer. Both these factors should combine to make any reaction of the cyclic thiolsulfinates that has to go through **7c**-H (or **8c**-H) as an intermediate less favorable kinetically than reactions involving **7b**-H (or **8b**-H) as intermediates. It is quite conceivable that the effect could be large enough that the actual disappearance of **5** or **6** in CN^-–HCN buffers will occur via some completely different pathway not involving **7c**-H or **8c**-H. As we will now see, this indeed can be the case.

In a 1:1 CN^-–HCN buffer containing 0.025 M CN^- (conditions where $k'_{CN}[CN^-]$ for **6** is 1.75 s^{-1}) thiosulfinate **6** (10^{-4} M) disappears only very slowly, with ~180 min being required for the first 50% of reaction. The kinetics of the disappearance of **6** under these conditions can be followed conveniently by monitoring the increase in the optical density of the solution at 367 nm, a wavelength where disulfide **10**, which is one of the major products of the decomposition of **6** under such conditions (vide infra), has a very strong absorption maximum (ϵ 12 000). The kinetic behavior of the disappearance of **6** in various CN^-–HCN buffers at varying $[CN^-]$ is shown in the first section of Table V. The following points should be noted: (1) the disappearance of **6** follows kinetics which are *second* order, rather than first-order in [**6**] (the only exception being the run at the highest cyanide ion concentration in the 1:1 buffer which shows a combination of a first- plus second-order dependence on [**6**]); (2) the rate constant (k_2) for this second-order reactin of **6** is *independent* of $[CN^-]$ but dependent on the buffer ratio, increasing linearly as $[CN^-]/[HCN]$ increases. This particular type of kinetic

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[10] In water the pK_a of HCN (9.31) is 2.4 pK units larger than pK_2 for H_2SO_3 (6.91). A comparable ΔpK_a seems likely in 60% dioxane.

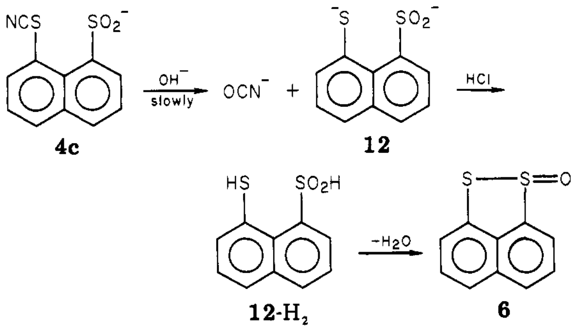
behavior is most easily explained by a mechanism of the type in eq 15, where I^- is some intermediate formed re-

$$\mathrm{OH^-} + \mathbf{6} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \mathrm{I^-} \qquad (15a)$$

$$\mathrm{I^-} + \mathbf{6} \xrightarrow{k_b} \mathrm{X} \rightarrow \rightarrow \rightarrow \text{products} \qquad (15b)$$

versibly by the reaction of **6** with hydroxide ion, and the rate-determining step is then the reaction of I^- with a second molecule of the thiolsulfinate (step k_b).

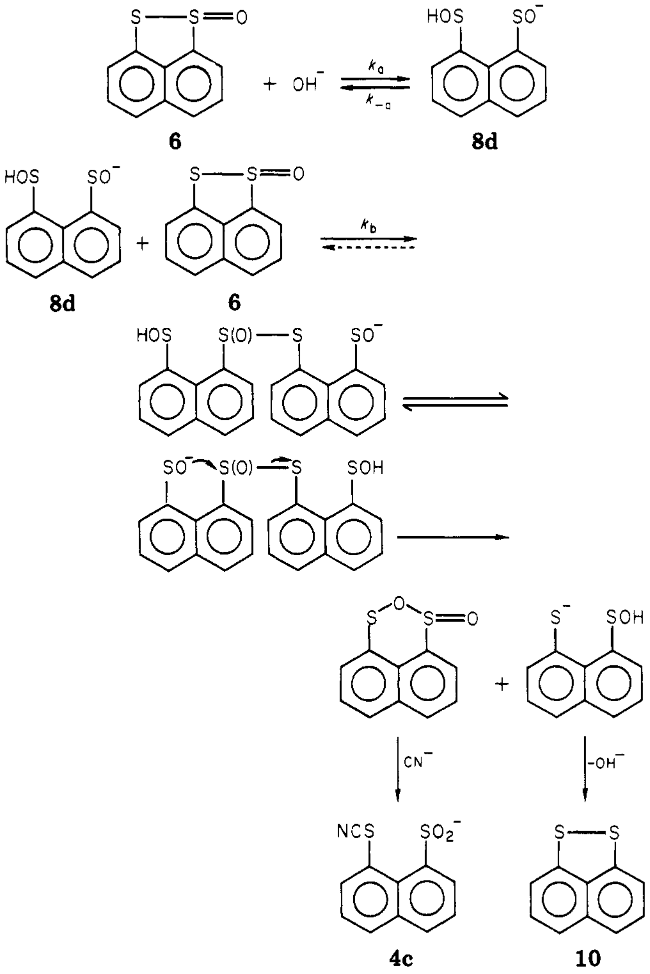
The products of this "second-order", OH^--promoted decomposition were investigated by allowing **6** (0.02 M) to decompose in a 60% dioxane solution containing 0.03 M each of CN^- and HCN. The major product, formed in a yield of ~0.5 mol/mol of **6** reacting, was the cyclic disulfide **10**. The yield of **10** was the same whether estimated from the optical density of a diluted aliquot of the final reaction solution at 367 nm (the wavelength where **10** has a strong absorption maximum) or by actual physical isolation of **10** by removal of dioxane from the final reaction solution, extraction of the water-insoluble products with benzene, and subsequent chromatography. Also isolated from the benzene extracts upon chromatography was thiolsulfonate **2** (0.25 mol/mol of **6**). Since **2** is known[1] to be converted almost quantitatively to **4c** in the presence of 0.02–0.03 M CN^-, the thiolsulfonate itself cannot be present in large concentration in the final reaction solution. It must be formed in some manner during the workup procedure. The most likely route would seem to be reversion of **4c** to **2** in the manner outlined in a footnote.[11] Acidification of the aqueous solution with HCl, after the extraction of the water-insoluble products, results in the rapid precipitation of thiolsulfinate **6** (0.17 mol/mol of **6** originally taken). Since **6** is completely insoluble in water, it cannot have been present in the aqueous solution prior to acidification. It must therefore arise from some other species when the solution is acidified. Previous work[1] has shown that on being allowed to stand in alkaline solution (CN–HCN buffer) **4c** slowly undergoes conversion to a species that generates thiosulfinate **6** when the solution is acidified. We now think that this species is probably **12**; this upon acidification with HCl will be protonated to **12**-H_2, which then undergoes rapid dehydration to afford **6** (eq 16).



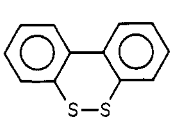
(16)

We therefore believe that in CN^-–HCN buffers the products of the "second-order", OH^--promoted decomposition of **6** are **10** and **4c**, in approximately equal amounts, with some of the **4c** then undergoing hydrolysis to **12** during the period of time (72 h) that the reaction solution was allowed to stand before the reaction was worked up.

Scheme II. Mechanism of OH^--Promoted Decomposition of 6 in Cyanide Buffers



In 4:1 or 2:1 CN^-–HCN buffers the cyclic six-membered thiolsulfinate **5** also disappears almost entirely as a result of an OH^--promoted reaction, as evidenced (Table V) by the fact that its rate of disappearance in such buffers is effectively independent of $[CN^-]$ but linearly dependent on the buffer ratio $[CN^-]/[HCN]$. The products of this reaction, analogous to those for the OH^--promoted decomposition of **6**, are equimolar amounts of cyclic disulfide **12** and **3c**. However, the OH^--promoted decomposition of **5** in these buffers exhibits kinetics that are *first* order in [**5**], rather than the second-order dependence on thiolsulfinate concentration found for the same reaction with **6**. This can be explained in terms of the type of kinetic scheme shown in eq 15 if for **5** $k_b[\mathbf{5}] > k_{-a}$, whereas for **6** $k_{-a} > k_b[\mathbf{6}]$. That this should be the case is not at all surprising provided the reaction of OH^- with the cyclic thiolsulfinates that gives I^- (step k_a) is a ring-opening reaction leading to the formation of either **7d** or **8d** (Nu = OH), because (based on the behavior of **3** and **4**[1,2]) the rate of reversion of **8d** to **6** (step k_{-a}) should probably be anywhere from 200 to 500 times faster than the rate of cor-



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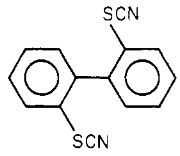

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[11] The workup procedure used for the removal of the dioxane and some of the water from the final reaction solution will result in much of the cyanide present originally being lost evaporatively as HCN. The equilibrium constant (K_{eq} = 660) for the **2** + CN^- ⇄ **4c** equilibrium is small enough so that in a dilute aqueous cyanide solution there will be some **2** present at equilibrium with **4c**. Since **2** is not soluble in water while **4c** is, **2** precipitates from such a solution, thereby displacing the equilibrium in a manner such that all **4c** reverts to **2** (k_{-CN} for **2** is 28 s^{-1}); the precipitated **2** is then extracted by the benzene.

responding reversion of **7d** to **5**.

In our opinion the most reasonable mechanism for the OH^--promoted decomposition of the cyclic thiolsulfinates in cyanide buffers would therefore seem to be the one shown for **6** in Scheme II. The same mechanism would apply for the reaction involving **5**, the only difference being that when the cyclic thiolsulfinate is **5**, step k_{-a} is slower, rather than faster, than the rate of reaction of the intermediate (**7**, Nu = OH) with the thiolsulfinate (step k_b). The mechanism in Scheme II satisfactorily accounts for both the products of the reaction and also for the difference in kinetic order in thiolsulfinate for the reaction of **5** as compared to **6**.

In 1:1 CN^-–HCN buffers the experimental first-order rate constant (k_1) for the disappearance of **5** (Table V) is the sum of the rate for the OH^--promoted decomposition plus a significant contribution from a rate term whose magnitude is dependent on cyanide concentration. The exact nature of the reaction responsible for the $[CN^-]$-dependent term is not clear at this time. There are definite indications, however, that it is apparently not analogous to the reaction of **5** with sulfite that results in the formation of **11**. Thus, examination of the reaction products produced under conditions (0.01 M **5**, 0.015 M CN^- and HCN) where the $[CN^-]$-dependent reaction should make a significant contribution to the total rate indicates that dithiocyanate **13** is not formed to any detectable extent, while the yield of disulfide **12** is somethat greater than that found in the OH^--promoted decomposition alone. Also, the dependence of rate on $[CN^-]$ in the range of cyanide concentrations up to 0.01 M suggests a predominantly first-order dependence of rate on cyanide concentration, rather than the second-order dependence on nucleophile concentration found in the sulfite reaction. Therefore what is being observed is in all probability a reaction where **7c**, rather than **7c**-H, is the important intermediate. However, until this aspect of the disappearance of **5** in 1:1 CN^-–HCN buffers can be studied in much more detail than was possible in the present work, further speculation about the exact nature of the process responsible for the $[CN^-]$-dependent terms does not seem warranted.

Experimental Section

Preparation and Purification of Materials. Dibenzo[*c*,*e*]-1,2-dithiin 1-Oxide. Dibenzo[*c*,*e*]-1,2-dithiin [**12**, mp 112–113 °C (lit.[12] mp 113 °C)] was synthesized from biphenyl-2,2′-disulfonyl dichloride[13] by the procedure outlined by Barber and Smiles,[12] with the modification that dioxane rather than ethanol was used as the solvent to dissolve the disulfonyl chloride prior to its reduction with zinc dust.

To 0.704 g of **12** dissolved in 50 mL of chloroform and kept at 0 °C was slowly added over the course of 1 h a solution of 0.625 g of 90% *m*-chloroperbenzoic acid in 50 mL of the same solvent. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stand for one additional hour. The chloroform solution was then washed three times with 5% sodium bicarbonate and dried ($MgSO_4$), and the chloroform was removed under reduced pressure. The residue was recrystallized from 1:2 benzene–hexane, giving 0.40 g (53%) of dibenzo[*ce*]-1,2-dithiin 1-oxide (**5**): mp 132–134 °C (lit.[14] mp 134–135 °C); IR (KBr) 3080, 1470, 1435, 1098 (S=O), 960, 760 cm^{-1}.

Naphtho[1,8-*cd*]-1,2-dithiole 1-Oxide. Naphtho[1,8-*cd*]-1,1-dithiole [**10**, mp 121–123 °C (lit.[15] mp 116 °C)] was oxidized with *m*-chloroperbenzoic acid in exactly the same manner as for **12**, giving naphtho[1,8-*cd*]-1,2-dithiole 1-oxide [**6**, mp 93–95 °C (lit.[14] mp 91–92 °C)] in 50% yield after recrystallization from 1:1 benzene–hexane: IR (KBr) 1475, 1390, 1200, 1070 (S=O), 800, 750 cm^{-1}.

Optically Active 5. Optically active percamphoric acid was prepared from (−)-camphoric anhydride: mp 227–231 °C (lit.[16] mp 223–224 °C); $[\alpha]_{436}$ −8.7° (*c* 3, benzene). Sodium peroxide (9.5 g, 0.12 mol) was dissolved in 100 mL of water and cooled to −5 °C. To this solution was then added 10.5 g (0.06 mol) of (−)-camphoric anhydride, and the mixture was stirred until all of the anhydride had dissolved (2–3 h). The solution was then acidified by the addition of ice-cold 50% sulfuric acid and extracted twice with 100-mL portions of chloroform. The chloroform extracts were dried ($MgSO_4$), and the chloroform was removed under reduced pressure. The residual viscous oil (8.2 g) was dissolved in 100 mL of reagent-grade chloroform, and the percamphoric acid concentration of the solution was determined by using the iodometric procedure described by Vogel.[17]

A solution of 2.87 mmol of optically active percamphoric acid in 50 mL of chloroform was added with stirring over the course of 2 h to a solution of **12** (0.62 g, 2.87 mmol) in 50 mL of the same solvent at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stand for 2 h. It was then extracted three times with 100-mL portions of 5% sodium bicarbonate and dried ($MgSO_4$), and the chloroform was removed under reduced pressure. The residue was crystallized from 1:1 benzene–hexane, giving 0.30 g (45%) of (−)-**5**: mp 134–136 °C; $[\alpha]_{436}$ −9.3° (*c* 0.5, 60% dioxane).

Optically Active 6. A sample of **10** (2.9 g, 15.2 mmol) was oxidized with 15.2 mmol of optically active percamphoric acid in the same manner as described for **12**. Recrystallization of the crude product from 1:1 benzene–hexane gave 1.24 g (40%) of (+)-**6**: mp 93–95 °C; $[\alpha]_{546}$ +8.3° (*c* 1.0, 60% dioxane).

Other Reagents. Dioxane was purified by the procedure described by Fieser and Fieser,[18] and the freshly fractionated distilled solvent was then frozen and stored at −20 °C to prevent the formation of peroxides prior to use. 2-Methyl-2-propanethiol (Aldrich) was purified by fractional distillation and stored under argon. All water used in kinetic runs was doubly distilled from glass. All other reagents used were of the highest degree of purity commercially available and were used without further purification.

Procedure for Kinetic Runs. The kinetics of the reactions of **5** and **6** in sulfite or cyanide buffers were followed by conventional ultraviolet spectrophotometry. The reactions were initiated by injection of 35 μL of a concentrated aqueous solution containing the appropriate concentrations of the nucleophile and its conjugate acid into 3.5 mL of a solution of the thiolsulfinate in 60% dioxane contained in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Cary Model 17 spectrophotometer. The change of optical density with time at an appropriate wavelength (**5**–sulfite, 265 nm; **5**–cyanide, 300 nm; **6**–sulfite, 343 nm; **6**–cyanide, 367 nm) was then followed.

The reaction of **5** with *t*-BuS^- was followed by stopped-flow spectrophotometry. A solution of **5** (9×10^{-5} M) in 60% dioxane was placed in one of the reservoir syringes of a Durrum Model D-110 stopped-flow spectrophotometer. Either a solution of 2-methyl-2-propanethiol in a borate buffer in 60% dioxane or a solution of *t*-BuS^- and *t*-BuSH in the same solvent, prepared by adding the proper amount of standard sodium hydroxide to a solution of the thiol in 60% dioxane, was placed in the other reservoir syringe. The two solutions were then mixed, and the change in the absorbance of the solution at 300 nm with the time was then monitored on a storage oscilloscope.

Kinetics of Racemization of Optically Active Thiolsulfinates. In the studies using sulfite or cyanide 5.5 mL of a solution of (−)-**5** (0.02 M) in 60% dioxane was placed in a thermostated, 1-dm polarimeter tube in the cell compartment of a Perkin-Elmer Model 141 spectropolarimeter. Then 55 μL of a concentrated aqueous solution containing the desired concen-

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trations of the nucleophile and its conjugate acid was injected into the solution in the polarimeter tube and mixed, and the decrease in the rotation of the solution with time was monitored at 436 nm. Prior to the addition of the solution of the nucleophile there was no change in the rotation.

The racemization of (1)-**6** (0.05 M) by added sulfite or cyanide was studied in exactly the same way. With (+)-**6** the wavelength at which the decrease in rotation was followed was 546 nm. The final rotation of the solutions was always zero.

To study the rate of racemization of (–)-**5** or (+)-**6** in the presence of 2-methyl-2-propanethiol in acetate buffers a slight modification of the procedure above was employed. The optically active thiolsulfinate was dissolved in 60% dioxane containing the proper amounts of sodium acetate and acetic acid, and this solution of the thiolsulfinate in the acetate buffer was placed in the polarimeter tube. A small amount (6.2 μL) of 2-methyl-2-propanethiol was then injected into this solution and thoroughly mixed, and the decrease in the rotation of the solution was followed. Prior to the addition of the thiol there was no change in the rotation of the solution with time, showing that the acetate buffer alone does not racemize either (–)-**5** or (+)-**6** at an appreciable rate.

Reaction of 6 with Sulfite. Sodium sulfite (0.16 g, 1.25 mmol), sodium metabisulfite (0.12 g, 0.62 mmol), and **6** (0.17 g, 0.84 mmol) were dissolved in 85 mL of 60% dioxane, and the solution was allowed to stand for 24 h at room temperature. The solution was then evaporated to dryness under reduced pressure, and the solid residue was extracted with two 25-mL portions of benzene. Evaporation of the benzene extracts afforded 0.064 g (0.34 mmol) of naphtho[1,8-*cd*]-1,2-dithiole (**10**), identical in all respects with a known sample. The solid residue was next shaken for 1 h with 50 mL of absolute methanol and filtered in order to remove sodium sulfite, which is insoluble in methanol, and the methanol filtrate was then evaporated to dryness under reduced pressure. In one experiment the residual solid was dissolved in 15 mL of water, and 0.19 g of potassium chloride was added. The solution was then cooled overnight, which resulted in the separation of crystals of a hydrate of the dipotassium salt of **9** (i.e., K replaces Na in **9**): mp >260 °C dec; IR (KBr) 3600, 3400, 1605, 1210 (SO_3^-, very strong) 1165, 1030, 1020, 830, 775 cm^{-1}. For quantitative estimation of the amount of **9** present, the residual solid (0.21 g) from another experiment was dissolved in 50 mL of water, 0.1 g of concentrated sulfuric acid was added, and the solution was heated to 50 °C for several hours. This led to the separation of 0.092 g (0.48 mmol) of **10**, identical in all respects with a known sample of this disulfide.

Decomposition of 6 in Cyanide Buffers. A solution of **6** (0.41 g, 2.0 mmol) in 60 mL of dioxane and 7.5 mL of aqueous 0.4 M HCl were mixed with a solution of 0.39 g (6 mmol) of potassium cyanide in 32.5 mL of water, and the resulting solution was allowed to stand at room temperature for 3 days. The solution was then evaporated to dryness under reduced pressure. Water (15 mL) was added to the residue, and the resulting mixture was extracted twice with 50-mL portions of a 1:1 mixture of benzene and chloroform. The benzene–chloroform extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. TLC indicated that the residue was a mixture of disulfide **10** and thiolsulfonate **2**. Column chromatography of the residue on silica gel with 2:1 hexane–benzene and benzene as eluents afforded pure **10** and **2**, identical in all respects with known samples, and no other compounds. The amounts of the two compounds in the residue were as follows: **10**, 0.199 g (1.05 mmol); **2**, 0.107 g (0.48 mmol).

The aqueous solution remaining after the benzene–chloroform extraction was acidified by the addition of HCl. Almost immediately a precipitate separated. This was shown to be **6**: 0.07 g (0.35 mmol); mp 93–94 °C (after recrystallization from benzene–hexane).

In another experiment the amount of **10** present in the reaction solution at the end of the reaction was estimated by taking a 17.5-μL aliquot of the final reaction solution, diluting it to 3.5 mL with 60% dioxane, and then measuring the optical density of the solution at 367 nm, the wavelength at which **10** has a strong absorption maximum (ϵ 12 200) but where the other products of the reaction are transparent. The measured optical density (0.59) indicated that the concentration of **10** in the final reaction solution was 9.82×10^{-3} M. This corresponds to a total of 0.982 mmol of **10** and shows that no significant amount of **10** is formed from other products during the workup of the reaction solution.

Decomposition of 5 in Cyanide Buffers. A solution of **5** (0.104 g, 0.50 mmol) in 30 mL of dioxane and 0.62 mL of aqueous 0.4 M HCl were added to a solution of 0.081 g (1.25 mmol) of potassium cyanide in 19.4 mL of water, and the resulting solution was allowed to stand for 3 h at room temperature. The final reaction solution was then worked up in the same general manner as in the reaction of **6** in cyanide buffers. Upon evaporation the benzene–chloroform extract afforded 0.054 g of material that was shown by chromatographic and spectroscopic procedures to be almost entirely a mixture of **12** (0.038 g, 0.20 mmol) and **1** (0.010 g, 0.046 mmol). Acidification (using HCl) of the aqueous solution remaining after the benzene–chloroform extraction resulted in the separation of **1** (0.036 g, 0.16 mmol), identical in all respects with a known sample of this thiolsulfonate.

In another experiment the same amount of **5** (0.104 g) was allowed to decompose in a 1:1 CN^-–HCN buffer in 60% dioxane (1.87 mL of 0.4 M HCl, 0.100 g of KCN; total volume of solution, 50 mL). After 3 h the same workup procedure afforded from the benzene–chloroform extract 0.074 g of material that was shown to contain 0.044 g (0.23 mmol) of **12** and 0.022 g (0.098 mmol) of **1**. No significant amount of a product having an IR spectrum consistent with the expected for **13** could be detected. Acidification of the aqueous solution remaining after the benzene–chloroform extraction led to the separation of 0.023 g (0.10 mmol) of **1**.

Acknowledgment. The support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Registry No. 5, 49833-13-8; (–)-**5**, 82280-76-0; **6**, 49833-12-7; (+)-**6**, 82280-77-1; **9**, 82280-78-2; *t*-BuS^-, 20733-19-1; SO_3^{2-}, 14265-45-3; CN^-, 57-12-5.