Reactivity of Cyclic Five- and Six-Membered Aryl α-Disulfones toward Nucleophiles

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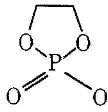
The rates of reaction of a cyclic five-membered aryl α-disulfone, naphtho[1,8-*cd*]-1,2-dithiole 1,1,2,2-tetroxide (7), and a six-membered compound, dibenzo[*ce*]-1,2-dithiin 1,1,2,2-tetroxide (8), with a variety of nucleophiles have been measured under the same conditions for which data are available on the rates of reaction of the nucleophiles with phenyl α-disulfone. In marked contrast to the behavior of the corresponding sultone, 1-naphthol-8-sulfonic acid sultone (5), which hydrolyzes 10^7 times faster than its open-chain analogue, α-disulfone 7 does not hydrolyze, or undergo any other nucleophilic substitution reactions, significantly faster than either phenyl α-disulfone or 8. Measurement of the heat of alkaline hydrolysis of 7 suggests that this may be due to the fact that, in contrast to the situation with sultone 5, there is no significant strain associated with the five-membered ring in 7. Although 7 reacts with many nucleophiles (OH^-, HO_2^-, CN^-, NH_2NH_2) at about the same rate as does phenyl α-disulfone, it reacts with cyclic secondary and tertiary amines from 200 to 800 times slower than does the open-chain α-disulfone. This is believed to be due to a steric effect in which in 7 an ortho position in the naphthalene ring interferes with the approach of more bulky nucleophiles to the sulfonyl group. With phenyl α-disulfone such interference can be avoided by appropriate rotation of a phenyl group.

Certain cyclic five-membered sulfates and sultones undergo hydrolysis from 10^5 to 10^7 times faster than their acyclic analogues.[2] The situation is reminiscent of the phenomena observed in the hydrolysis of cyclic five-membered phosphates and phostonates.[3] Thus, just as methyl ethylene phosphate, 1, hydrolyzes about 10^6 faster than trimethyl phosphate, 2, so catechol sulfate, 3, hydrolyzes 2×10^7 faster than diphenyl sulfate, 4.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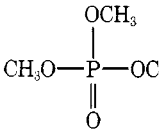
$\mathrm{CH_3O{-}P(OCH_3)(=O){-}OCH_3}$

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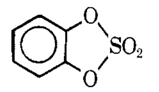
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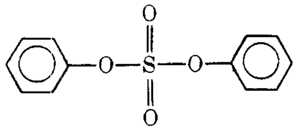
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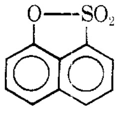
In the case of the phosphorus derivatives, Westheimer[3] has made a convincing case that the rate acceleration is due to a relief of strain in the five-membered ring that occurs on going from the starting ester to a trigonal-bipyramidal intermediate in which the ring spans an apical and radial position. Data on the heat of hydrolysis[4] and x-ray studies of their structure[5] suggest that a comparable amount of ring strain is present in cyclic five-membered sulfates and sultones. The natural inference is that the large rate accelerations observed for the five-membered sulfates and sultones also have their origin in the relief of strain that occurs on going from the starting ester to a trigonal-bipyramidal intermediate (or transition state) in which the five-membered ring spans an apical and a radial position.

One of the five-membered cyclic sultones that undergoes hydrolysis much faster than an open-chain sultone is 1-naphthol-8-sulfonic acid sultone (5). Kaiser, Kudo, and Zaborsky[2c] showed that 5 hydrolyzes in alkaline solution 2.5×10^7 times faster than diphenyl sulfate (4) and 5×10^5 times faster than phenyl α-toluenesulfonate (6). From ^{18}O-labeling experiments on closely related substrates,[6] hydrolysis of 5 is known to take place via S–O bond cleavage, so that the large rate enhancement observed for this compound is definitely associated with an enhanced rate of substitution at the sulfonyl sulfur.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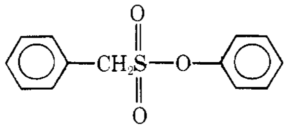
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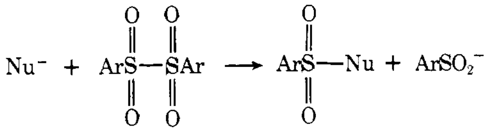
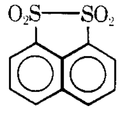
In recent years we have studied extensively[7] nucleophilic substitution reactions of aryl α-disulfones. These can be represented generally as shown in eq 1 and are obviously reactions that, like the hydrolysis of 5, involve nucleophilic substitution at the sulfonyl sulfur.


$$\mathrm{Nu^- + ArS(=O)_2{-}S(=O)_2Ar \longrightarrow ArS(=O)_2{-}Nu + ArSO_2^-} \qquad (1)$$

We were interested in whether or not hydrolysis and other nucleophilic substitution reactions of naphtho[1,8-*cd*]-1,2-dithiole 1,1,2,2-tetroxide (7), the cyclic five-membered α-disulfone analogous to 5, would show the same sort of very large rate accelerations relative to phenyl α-disulfone, $PhSO_2SO_2Ph$ (9), as one observes for sultone 5 relative to open-chain aryl sulfonates.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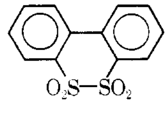
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While examining the rates of reaction of 7 with various nucleophiles we have also looked at the rates of reaction of the cyclic six-membered α-disulfone dibenzo[*ce*]-1,2-dithiin 1,1,2,2-tetroxide (8) with many of the same nucleophiles. In the case of sulfates and sultones, cyclic six-membered compounds, in marked contrast to the behavior of five-membered ones, do *not* hydrolyze at appreciably faster rates than their acyclic analogues.

Results

The synthesis of α-disulfones 7 and 8 is outlined in an accompanying paper.[8] The kinetics of their reactions with nucleophiles at 25 °C in 60% dioxane as solvent were followed spectrophotometrically (either conventional or stopped-flow)

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Table I. Kinetics of the Reaction of Anionic Nucleophiles with 7 and 8 in 60% Dioxane at 25 °C

α-Disulfone, concentration (M)	Nucleophile	$[Nu^-]$, M	[NuH], M	k_1, s^{-1}	$k_{Nu} = k_1/[Nu^-]$, $M^{-1} s^{-1}$
7, 2.2×10^{-4}	OH^-	0.10		19.7	2.0×10^2
		0.08		15.9	2.0×10^2
		0.06		11.7	2.0×10^2
		0.04		8.0	2.0×10^2
		0.02		3.8	1.9×10^2
1.0×10^{-4}	CN^-	*a*	*a*	*a*	8.0
2.7×10^{-4}	HO_2^-	0.002	0.0165	12.7	6.4×10^3
8, 1.1×10^{-4}	OH^-	0.04		9.4	2.4×10^2
		0.02		4.7	2.4×10^2
1.4×10^{-4}	CN^-	*a*	*a*	*a*	3.5
1.3×10^{-4}	HO_2^-	0.004	0.016	59.8	1.5×10^4
		0.002	0.018	28.1	1.4×10^4
	OCl^-	0.002		2.87	1.4×10^3
		0.001		1.36	1.4×10^3

[a] For data for individual runs see Table III of ref 8.

Table II. Kinetics of the Reaction of Various Nitrogen Bases with 7, 8, and Phenyl α-Disulfone in 60% Dioxane at 25 °C

α-Disulfone, concentration (M)	Nucleophile	[Nu], M	$[NuH^+]$, M	$k_1 \times 10^2$, s^{-1}	$k_{Nu} = k_1/[Nu]$, $M^{-1} s^{-1}$
7, 1.0×10^{-4}	Piperidine	0.016	0.016	0.77	0.48
		0.008	0.008	0.39	0.49
	Piperazine	0.016	0.016	0.38	0.24
		0.008	0.008	0.167	0.21
	Morpholine	0.08	0.08	0.194	0.024
			0.04	0.205	0.026
		0.04	0.04	0.109	0.026
		0.02	0.02	0.046	0.023
			0.01	0.047	0.024
	Quinuclidine	0.10	0.10	1.27	0.127
	3-Quinuclidinol	0.08	0.08	0.234	0.029
		0.04	0.04	0.112	0.028
	Triethylenediamine	0.08	0.08	0.109	0.0136
	(Dabco)	0.04	0.04	0.055	0.0137
		0.08	0.08	0.068 (D_2O)	0.0084
		0.04	0.04	0.034 (D_2O)	0.0084
	NH_2NH_2	0.0106	0.010	2.66	2.52
		0.00422	0.0040	1.07	2.53
8, 1.1×10^{-4}	Morpholine	0.04	0.04	5.3	1.33
		0.02	0.02	2.6	1.30
1.0×10^{-4}	Triethylenediamine	0.08	0.08	0.52	0.066
	(Dabco)	0.04	0.04	0.25	0.063
9, 4.2×10^{-5}	Quinuclidine	0.0040	0.0043	39.0	98
		0.0020	0.0022	18.6	93
	3-Quinuclidinol	0.0025	0.0025	6.05 ± 0.01	24.4
	Triethylenediamine	0.010	0.010	11.5	11.5
	(Dabco)	0.0050	0.0050	16.13	12.3

under conditions where the nucleophile was always present in large stoichiometric excess over the α-disulfone so that the disappearance of the α-disulfone followed first-order kinetics. The reactions involving **8** were followed at its long wavelength absorption maximum, 313 nm. In the case of **7**, however, reaction with nucleophiles is not generally accompanied by much change in the absorbance at the long wavelength absorption maximum of **7** (302 nm), and so wavelengths in the region 320–335 nm were used.

The reactions of **7** and **8** investigated consisted of the following: (a) reaction with a group of nitrogen bases; (b) reaction with a group of common anionic nucleophiles; (c) the spontaneous hydrolysis of **7**. The reactions involving the nitrogen bases were all studied in buffers (usually 1:1) of the nitrogen base and its conjugate acid. Some of the reactions involving the anionic nucleophiles were also studied in buffers of the nucleophile, Nu^-, and its conjugate acid, NuH. Certain of the nitrogen bases examined, namely, quinuclidine and related cyclic tertiary amines, were ones for which kinetic data had not been previously obtained for phenyl α-disulfone. For this reason the reactivity of these particular tertiary amines toward $PhSO_2SO_2Ph$ was also determined, along with their reactivity toward **7**, in the present work.

The data for the runs involving the anionic nucleophiles and **7** and **8** are summarized in Table I, while the results for the nitrogen-base nucleophiles and the different α-disulfones are given in Table II. The data for the spontaneous hydrolysis of **7** are given in Table III. In each case, k_1 is the experimental first-order rate constant for the disappearance of the α-disulfone under the reaction conditions in question.

That all of the reactions in Tables I and II are first order in nucleophile is shown by the fact that for any given α-disulfone–nucleophile system k_1/[nucleophile] is independent of nucleophile concentration. Second-order rate constants, $k_{Nu} = k_1$/[nucleophile], for each system studied are also tabulated in Tables I and II.

Table III. Kinetics of the Spontaneous Hydrolysis of Naphtho[1,8-*cd*]-1,2-dithiole 1,1,2,2-Tetroxide (7) in 60% Dioxane[a]

Temp, °C	$k_1 \times 10^4$, s^{-1} [b]	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu
94.0	2.31 ± 0.01		
90.0	1.81 ± 0.01		
80.0	1.01 ± 0.03	14.6	−37.8
69.5	0.62 ± 0.06		
59.7	0.29 ± 0.01		

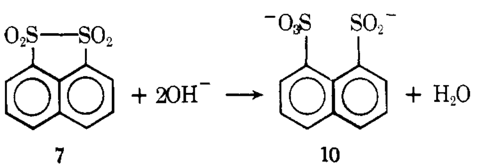
[a] All runs were in the presence of 0.01 M $HClO_4$. Other experiments showed that perchloric acid concentrations up to 0.1 M had no effect on the rate. [b] All results are the average of several runs.

Discussion

Table IV gives the rate constants for the reaction of the various nucleophiles with both the five-membered (7) and the six-membered (8) cyclic α-disulfones. For each case it also indicates the reactivity of the cyclic α-disulfone compared to that of phenyl α-disulfone, i.e., $k_7/k_{(PhSO_2)_2}$ or $k_8/k_{(PhSO_2)_2}$.

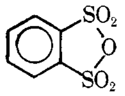
From inspection of the table it is at once apparent that *in no case* does the cyclic five-membered α-disulfone react much faster than phenyl α-disulfone. The dramatic rate accelerations observed by Kaiser and co-workers[2c] with the analogous cyclic sultone 5 are simply not seen with 7. Only in one case, that of reaction with cyanide ion, does the cyclic five-membered α-disulfone react more than 10 times faster than the open-chain compound, and even there the size of $k_7/k_{(PhSO_2)_2}$, 18, is many orders of magnitude smaller than the 10^5–10^7 rate accelerations characteristic of cyclic five-membered sulfates and sultones.

We noted earlier that the large rate accelerations observed[2] with 5 and with cyclic five-membered sulfates are believed to be due to the existence of significant strain in the cyclic substrates, which is relieved on going to a trigonal-bipyramidal intermediate or transition state. The lack of any rate acceleration for cyclic α-disulfone 7 would thus seem to suggest that either there is no significant strain associated with the α-disulfone ring in 7 or else that going from reactant to transition state (or intermediate) in the α-disulfone reactions for some reason does not lead to relief of strain in the way that it does for the substitution reactions of cyclic sulfates and sultones. We have measured the $\Delta H°$ (−54.2 kcal/mol) associated with the alkaline hydrolysis of 7 (eq 2) and find it to be slightly over 3 kcal/mol *smaller* than $\Delta H°$ (−57.3 kcal/mol) for the alkaline hydrolysis of phenyl α-disulfone:[9] $PhSO_2SO_2Ph + 2OH^- \rightarrow PhSO_2^- + PhSO_3^- + H_2O$. Unfortunately, since we do not know to what extent reaction product **10** is destabilized thermochemically due to interference between the sulfonate and sulfinate groups in the 1 and 8 positions,[10] we cannot say definitely that the smaller heat of alkaline hydrolysis of **7** compared to phenyl α-disulfone proves that there is little or no strain in the α-disulfone ring of **7**. However, given this caveat, the results do seem to suggest that the lack of rate acceleration for the cyclic five-membered α-disulfone is because there is not the strain associated with the five-membered ring in **7** that one finds in the corresponding sultone **5**.


(2)

7 **10**

α-Disulfone **7** is not the only cyclic five-membered sulfonyl derivative that does not show a marked rate acceleration compared to its acyclic analogue. Thus, Laird and Spence[12] have found that the solvolysis rates of the two cyclic sulfonic anhydrides **11** and **12** are not greatly different from their open-chain analogues.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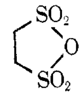
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Although no nucleophiles studied react with **7** much faster than they do with $PhSO_2SO_2Ph$, the cyclic secondary and tertiary amines in Table IV all react much slower (factor of 200 to 800). One should note, however, that this very marked reduction in rate is not seen with all nitrogen bases; the reactivity of hydrazine toward **7** is only a modest factor of six smaller than its reactivity toward phenyl α-disulfone, rather than the much larger factor of 200–800 observed with the cyclic amines.

Ritchie and co-workers[13] have examined the reactivity of a wide range of nucleophiles toward a pair of carbonium ions that differ significantly in the degree of steric hindrance they present to the approach of a nucleophile to their electrophilic center. Their results indicate that the reactivity of cyanide ion, hydrogen peroxide anion, and hydrazine (which they term "unhindered nucleophiles") is not affected by the increased steric hindrance at the reaction center of the more hindered carbonium ion; on the other hand, the relative reactivity of morpholine, piperidine, and piperazine is very significantly reduced.

Given Ritchie's findings,[13] we believe that a steric effect is almost certainly the correct explanation for the low reactivity

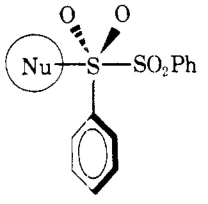
Table IV. Reactivity of Cyclic Five- and Six-Membered Aryl α-Disulfones toward Nucleophiles[a]

Nucleophile	Registry no.	5-Membered k_7,[b] $M^{-1} s^{-1}$	5-Membered $k_7/k_{(PhSO_2)_2}$	6-Membered k_8,[c] $M^{-1} s^{-1}$	6-Membered $k_8/k_{(PhSO_2)_2}$
OH^-	14280-30-9	200	2.6	240	3.2
HO_2^-	14691-59-9	6.4×10^3	1.1	1.5×10^4	2.8
CN^-	57-12-5	8.0	18	3.5	7.8
OCl^-	14380-61-1			1.4×10^3	1.8
Spontaneous hydrolysis (80 °C)		1.0×10^{-4}	1.0		
Piperidine	110-89-4	0.49	0.0041		
Piperazine	110-85-0	0.23	0.0048		
Morpholine	110-91-8	0.025	0.0021	1.3	0.11
NH_2NH_2	302-01-2	2.5	0.16		
Quinuclidine	100-76-5	0.13	0.0013		
3-Quinuclidinol	1619-34-7	0.029	0.0012		
Triethylenediamine (Dabco)	280-57-9	0.014	0.0011	0.065	0.0055

[a] All data are for 60% dioxane as solvent at 25 °C, except the spontaneous hydrolysis of 7 where data are at 80 °C. [b] Registry no.: **7**, 62609-77-2. [c] Registry no.: **8**, 64728-07-0.

of the cyclic secondary and tertiary amines toward 7 as compared to their reactivity toward $PhSO_2SO_2Ph$. Such an explanation is, of course, consistent with the fact that the reactivity toward 7 of unhindered nucleophiles like NH_2NH_2, CN^-, and HO_2^- is not greatly different than their reactivity toward the open-chain α-disulfone.

The substitution reactions of the α-disulfones presumably go through an intermediate (or transition state) in which the reacting nucleophile and the departing sulfinate ion occupy the apical positions of a trigonal bipyramid. In the case of the open-chain α-disulfones it is possible to rotate the phenyl group attached to the sulfonyl group undergoing substitution in such a way that it will present a minimum of hindrance to an incoming nucleophile (see structure 13). On the other hand, the structure of 7 is such that the ortho position to the point of attachment of the sulfonyl group will inevitably interfere (see structure 14) with the approach of any nucleophile that has significant steric requirements.



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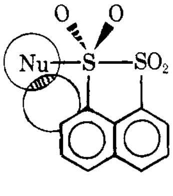

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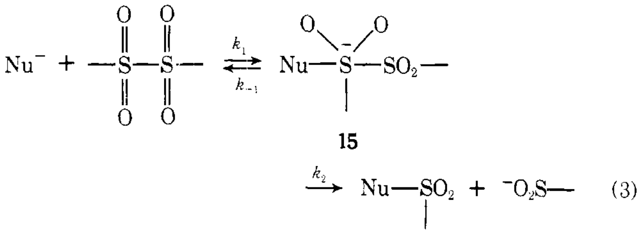
Let us now discuss briefly an alternative explanation for the low reactivity of 7 toward cyclic secondary and tertiary amines which was carefully considered but rejected as being inconsistent with certain aspects of the experimental results. Assume that the substitutions involving α-disulfones take place by a mechanism where an intermediate (15) is present on the reaction coordinate and which can be formulated generally as shown in eq 3. In analogous substitutions of carboxylic acid derivatives, Gravitz and Jencks[14] have shown that k_{-1} for amines ($Nu^- = {>}N{:}$) is 10^5 times larger than k_{-1} for oxyanions ($Nu^- = -O^-$) of equivalent basicity. If one were to assume that k_2 for cyclic α-disulfone 7 was much smaller than k_2 for phenyl α-disulfone, then one could conceivably have the following situation: with $PhSO_2SO_2Ph$ as the substrate k_2 for 15 would be larger than k_{-1} for all nucleophiles in Table IV, and for the open-chain α-disulfone k_1 (the attack of the nucleophile on the α-disulfone) would be rate-determining; on the other hand, with cyclic α-disulfone 7, although one would still have $k_2 > k_{-1}$ for nucleophiles like OH^-, HO_2^-, and CN^-, with the amines, where k_{-1} was much larger, one could have the opposite situation where $k_2 \ll k_{-1}$, and the measured rate constant, which would now be given by $k_1(k_2/k_{-1})$, could be much smaller than that found for phenyl α-disulfone, even though k_1 had essentially the same value as for the open-chain compound.

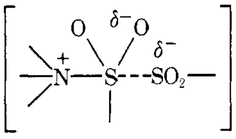


$$\mathrm{Nu^- + -\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Nu-\overset{O\diagdown\ -\diagup O}{\underset{|}{S}}-SO_2-}$$

15

$$\mathrm{\xrightarrow{k_2} Nu-\underset{|}{SO_2} + {}^-O_2S-} \qquad (3)$$

Such an explanation is at variance with several aspects of the experimental results, however. First, if in the reactions of the amines k_1 were rate determining for their reactions with phenyl α-disulfone while k_2 were rate determining for their reactions with 7, one would expect that β_{nuc} (from a plot of log k_{amine} vs. pK_a of amine H^+) should be much larger for the reactions involving 7 and the amines than for those involving phenyl α-disulfone; β_{nuc} is, of course, proportional to the amount of positive charge on the nitrogen atom in the rate-determining transition state and should therefore be much larger for a case where step k_2 is rate determining and the transition state is given by 16 than in a case where step k_1 is rate determining and the transition state resembles 17.[15] The actual β_{nuc} values for the different α-disulfone-amine reactions are as follows: $PhSO_2SO_2Ph$ with cyclic secondary amines, 0.39, with cyclic tertiary amines, 0.51; 7 with cyclic secondary amines, 0.50, with cyclic tertiary amines, 0.53. Clearly one does not see the large increase in β_{nuc} for the reactions of 7 that would be required by the proposed explanation. The fact that hydrazine reacts almost as rapidly with 7 as it does with phenyl α-disulfone, even though the cyclic secondary and tertiary amines do not, is also not in accord with an explanation based on the mechanism in eq 3 and a change in the rate-determining step for the reaction of amines with 7, since such an explanation would predict the hydrazine-7 reaction should be as markedly retarded as those of the other amines in Table IV. For these reasons we consider that this explanation can be rejected in favor of the one involving steric retardation of the reaction of cyclic amines with 7 outlined earlier.



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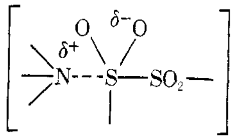

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The reaction of the cyclic tertiary amines with phenyl α-disulfone definitely involves nucleophilic attack by the amine and not general base catalysis by the amine of the attack of water on the α-disulfone. The clear evidence for this is the fact that the rate constant for the reaction of 3-quinuclidinol with $PhSO_2SO_2Ph$ is approximately 10^3 times larger than that for triethylamine,[16] even though the latter tertiary amine is about a factor of 10 stronger base. One might wonder, however, in view of the markedly lower rates of reaction of the cyclic tertiary amines with 7, whether these reactions still involve nucleophilic attack or whether, alternatively, one now has general base catalysis by the amine. Two considerations lead us to believe that nucleophilic attack is still involved, despite the low rates. First, the β value associated with the reaction of the cyclic tertiary amines with 7 is the same within experimental error as the β value associated with their reaction with phenyl α-disulfone, where we know that nucleophilic attack by the amine is involved. Second, we have measured the solvent isotope effect associated with the reaction of Dabco with 7, and the value we find, $k_{H_2O}/k_{D_2O} = 1.6$, is below the range of 1.9-4.4, typical of reactions where amines act as general base catalysts.[17] Earlier work[16b,18] has found solvent isotope effects of about 1.4 for reactions in 60% dioxane involving sulfur substrates in which tertiary amines act as nucleophilic catalysts.

Experimental Section

Preparation and Purification of Materials. The preparation of naphtho[1,8-*cd*]-1,2-dithiole 1,1,2,2-tetroxide (7) and dibenzo[*ce*]-1,2-dithiin 1,1,2,2-tetroxide (8) is described in an accompanying paper.[8] Triethylenediamine (Aldrich) was purified by recrystallization from benzene-hexane. Dioxane was purified by the procedure of Hess and Frahm[19] and was then stored frozen at −20 °C to prevent formation of peroxides prior to use. Piperidine, morpholine, piperazine, and phenyl α-disulfone were purified as outlined by Kice and Legan.[7a] For all the other reagents the highest purity commercially available material was used without further purification.

Procedure for Kinetic Runs. Depending on the rapidity of the particular reaction, either conventional or stopped-flow spectrophotometry was used to follow the kinetics. For the runs in Tables I and II the general procedures used were those already outlined in 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.

References and Notes

(1) (a) Texas Tech University; (b) University of Vermont.
(2) (a) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *J. Am. Chem. Soc.*, **87**, 3781 (1965); (b) O. R. Zaborsky and E. T. Kaiser, *ibid.*, **88**, 3084 (1966); (c) E. T. Kaiser, K. Kudo, and O. R. Zaborsky, *ibid.*, **89**, 1393 (1967).
(3) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968).
(4) E. T. Kaiser, M. Panar, and F. Westheimer, *J. Am. Chem. Soc.*, **85**, 602 (1963).
(5) (a) F. P. Boer and J. J. Flynn, *J. Am. Chem. Soc.*, **91**, 6604 (1969); (b) F. P. Boer, J. J. Flynn, E. T. Kaiser, O. R. Zaborsky, D. A. Tomalia, A. E. Young, and Y. C. Tong, *ibid.*, **90**, 2970 (1968); (c) E. B. Fleischer, E. T. Kaiser, P. Langford, S. Hawkinson, A. Stone, and R. Dewar, *Chem. Commun.*, 197 (1967).
(6) E. T. Kaiser and O. R. Zaborsky, *J. Am. Chem. Soc.*, **90**, 4626 (1968).
(7) (a) J. L. Kice and E. Legan, *J. Am. Chem. Soc.*, **95**, 3912 (1973); (b) J. L. Kice, G. J. Kasperek, and D. Patterson, *ibid.*, **91**, 5516 (1969); (c) J. L. Kice and G. J. Kasperek, *ibid.*, **91**, 5510 (1969); (d) J. L. Kice, *J. Org. Chem.*, **37**, 1865 (1972).
(8) M. M. Chau and J. L. Kice, *J. Org. Chem.*, **43**, companion paper in this issue.
(9) J. L. Kice, H. C. Margolis, W. S. Johnson, and C. A. Wulff, *J. Org. Chem.*, **42**, 2933 (1977).
(10) Thermochemical destabilization, as a result of interference between substituents at the 1 and 8 positions, has been established in the case of 1,8-dimethylnapthalene.[11] In that case it has been estimated to amount to around 7 kcal/mol.
(11) W. D. Good, *J. Chem. Thermodyn.*, **5**, 715 (1973).
(12) R. M. Laird and M. J. Spence, *J. Chem. Soc. B.*, 1434 (1971).
(13) C. D. Ritchie, R. J. Minasz, A. A. Kamego, and M. Sawada, *J. Am. Chem. Soc.*, **99**, 3747 (1977).
(14) N. Gravitz and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 499 (1974).
(15) A. C. Satterthwait and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 7018 (1974).
(16) (a) J. L. Kice and G. J. Kasperek, *J. Am. Chem. Soc.*, **92**, 3393 (1970); (b) J. L. Kice, C. A. Walters, and S. B. Burton, *J. Org. Chem.*, **39**, 346 (1974).
(17) S. L. Johnson, *Adv. Phys. Org. Chem.*, **5**, 281 (1967).
(18) J. L. Kice and J. D. Campbell, *J. Org. Chem.*, **36**, 2291 (1971).
(19) K. Hass and H. Frahm, *Chem. Ber.*, **71**, 2627 (1938).

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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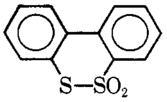
The cyclic thiolsulfonates dibenzo[*ce*]-1,2-dithiin 1,1-dioxide (1) and naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide (4) react rapidly in aqueous dioxane with excess cyanide or sulfite to undergo opening of the thiolsulfonate ring with formation (from reaction with CN$^-$) of thiocyanates (8 and 10, respectively) 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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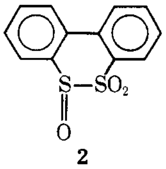

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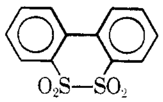

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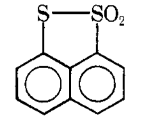

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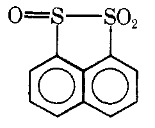

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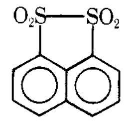

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