The Anomalous Course of the Reduction of Diphenyl-2,2'-disulfonyl Chloride. An Old Mystery Reexamined and Explained

Michael M. Chau and John L. Kice*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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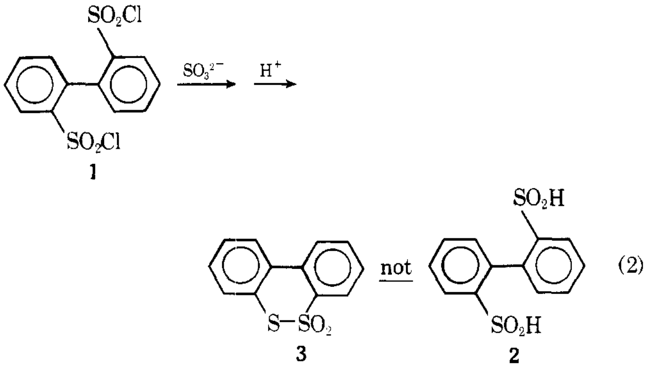
It has been known for many years that the reduction of diphenyl-2,2'-disulfonyl chloride (1) with sodium sulfite, followed by acidification of the reaction solution, gives not the expected diphenyl-2,2'-disulfinic acid (2), but rather the cyclic thiolsulfonate 3; the reasons for this anomalous behavior have, however, remained a mystery. We have now shown unambigously that the sequence of events involved in the conversion of 1 to 3 is as follows: (1) reduction of 1 with excess sulfite leads, as expected, to disodium diphenyl-2,2'-disulfinate (2-Na); (2) acidification of the aqueous reaction mixture containing 2-Na leads to the initial separation of disulfinic acid 2 as a second phase; (3) in this second phase the equilibrium constant for the formation of the cyclic sulfinyl sulfone 11 from 2 is large enough so that at equilibrium a considerable fraction of the disulfinic acid is present as 11; (4) once formed, the cyclic sulfinyl sulfone 11 is reduced to 3 by the excess sulfite (now present as H_2SO_3 and $NaHSO_3$) left over from the original reduction of 1. A similar sequence of reactions is thought also to be involved in those reductions of other disulfonyl chlorides by sulfite that have been reported (ref 2) to lead to cyclic thiolsulfonates rather than disulfinic acids. One also predicts that formation of a cyclic thiolsulfonate, rather than a disulfinic acid, will be the end result of the sulfite reduction of any other disulfonyl chlorides where the equilibrium constant for formation of the cyclic sulfinyl sulfone from the disulfinic acid is sufficiently favorable.

One of the standard synthetic routes for the preparation of aromatic sulfinic acids is the reduction of the corresponding sulfonyl chloride with excess sodium sulfite in a weakly alkaline solution, followed by acidification of the resulting solution to convert the aromatic sulfinate to the sulfinic acid; the sulfinic acid normally precipitates from the final solution.

$$ArSO_2Cl \xrightarrow{\text{excess } SO_3^{2-}} ArSO_2^- \xrightarrow{H^+} ArSO_2H \qquad (1)$$

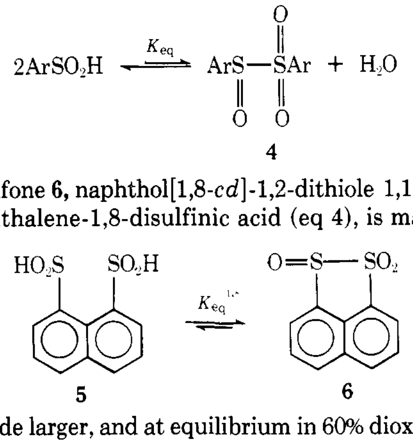
In 1928 Barber and Smiles[1] reported that when diphenyl-2,2'-disulfonyl chloride (1) was reduced with sulfite and the solution subsequently acidified, what was isolated was not the expected diphenyl-2,2'-disulfinic acid (2), but rather the cyclic thiolsulfonate 3, dibenzo [*c*,*e*]-1,2-dithiin 1,1-dioxide (eq 2).



(2)

A similar result was obtained in 1956 by Armarego and Turner[2a] upon reduction of the closely related compound 4,4',6,6'-tetramethyldiphenyl-2,2'-disulfonyl chloride with sulfite, and a year later the same workers[2b] also reported another instance where reduction of an aromatic disulfonyl chloride with sulfite led eventually to a cyclic thiolsulfonate. Although the anomalous behavior of 1 and related disulfonyl chlorides upon reduction with sulfite has thus been known for many years, the reasons for it have remained unknown.

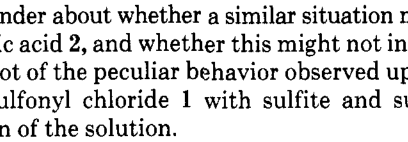
Recent work by Kice and Margolis[3] has revealed that, while the equilibrium constant for formation of the corresponding sulfinyl sulfone 4 from ordinary aromatic sulfinic acids (eq 3) in 60% aqueous dioxane is so small that the concentration of sulfinyl sulfone present at equilibrium is undetectable (<0.01%), the equilibrium constant for formation of the cyclic



$$2ArSO_2H \overset{K_{eq}}{\rightleftharpoons} ArS(=O)_2-S(=O)Ar + H_2O \qquad (3)$$

4

sulfinyl sulfone 6, naphthol[1,8-*cd*]-1,2-dithiole 1,1,2-trioxide, from naphthalene-1,8-disulfinic acid (eq 4), is many orders



5 6 (4)

of magnitude larger, and at equilibrium in 60% dioxane almost 75% of the material is present as the sulfinyl sulfone.

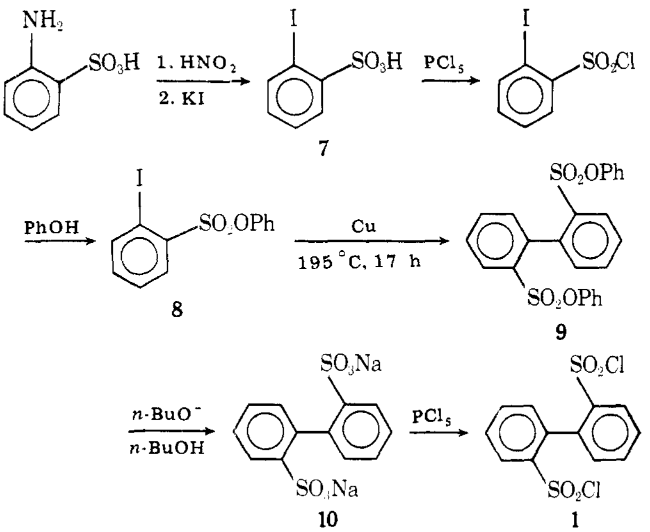
This demonstration that with appropriately structured disulfinic acids the cyclic sulfinyl sulfone can be strongly favored over the disulfinic acid, even in highly aqueous media, led us to wonder about whether a similar situation might exist for disulfinic acid 2, and whether this might not in some way lie at the root of the peculiar behavior observed upon reduction of disulfonyl chloride 1 with sulfite and subsequent acidification of the solution.

We therefore decided to carry out a careful reinvestigation of the system originally studied by Barber and Smiles[1] in order to find out exactly how cyclic thiolsulfonate 3 arose. The present paper describes the results of that study and outlines the solution to the almost 50-year-old mystery of the origin of 3. The nature of the explanation is such as to suggest that it is also in general applicable to the disulfonlyl chlorides studied by Armarego and Turner.[2] It also suggests that similar anomalous behavior upon sulfite reduction is likely to be encountered with many other appropriately structured disulfonyl chlorides.

Results and Discussion

Synthesis of Diphenyl-2,2'-disulfonyl Chloride. The synthesis of disulfonyl chloride 1 is outlined in Scheme I. Despite numerous attempts we were unable to repeat the reported[1] coupling of iodosulfonic acid 7 directly to 10. We therefore resorted to the type of route for coupling used by Armarego and Turner,[2] converting 7 to its phenyl ester 8 and

Scheme I. Synthesis of Diphenyl-2,2′-disulfonyl Chloride



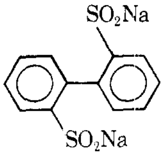
then coupling this to give **9** in good yield (77%), using copper powder at an elevated temperature. Treatment of **9** with excess sodium *n*-butoxide in *n*-butyl alcohol gave **10**; this was converted to the desired disulfonyl chloride **1** using phosphorus pentachloride.

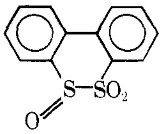
The melting point of the **1** which we obtained (144–145 °C) was somewhat higher than that reported by Barber and Smiles[1] (138 °C). However, the various spectral and analytical data for our material left no doubt that it was in fact **1**; the compound prepared by Barber and Smiles[1] was therefore apparently somewhat impure.

Reduction of Diphenyl-2,2′-disulfonyl Chloride with Sodium Sulfite. Upon heating a suspension of disulfonyl chloride **1** in a weakly alkaline aqueous solution containing a 25-fold excess of sodium sulfite, the disulfonyl chloride gradually dissolves and a colorless, clear solution results. Acidification of this solution with sulfuric acid to a pH of <1 causes the solution quickly to become cloudy as a second phase separates. If the mixture is warmed briefly, the cloudy suspension coagulates to a well-defined precipitate which, when filtered off, proves to be pure **3**, and is obtained in 93% yield. It is thus clear that **1** yields **3** quantitatively. No significant amount of any other organic product is formed.

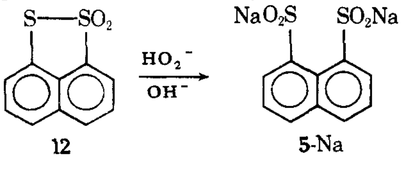
The cyclic thiolsulfonate **3** has a relatively sharp, long-wavelength absorption maximum, λ_{max} 296 nm (ϵ 8.7 × 10³), which is useful in distinguishing it from the other compounds to be encountered in this study.

Preparation of Disodium Diphenyl-2,2′-disulfinate and the Cyclic Sulfinyl Sulfone Derived from Diphenyl-2,2′-disulfinic Acid. To investigate the details of the conversion of **1** to **3** we had to have pure samples of both disodium diphenyl-2,2′-disulfinate (**2**-Na) and the cyclic sulfinyl sulfone (**11**) derived from diphenyl-2,2′-disulfinic acid.

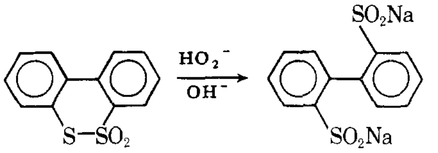

2-Na


11

Previous work by Kice and Margolis[3] has shown that disodium naphthalene-1,8-disulfinate (**5**-Na) can be prepared in quantitative yield by reaction of the cyclic thiolsulfonate **12** with hydrogen peroxide anion (eq 5). Treatment of cyclic thiolsulfonate **3** with 1 mol each of HO_2^- and OH^- in aqueous dioxane at room temperature led to the formation of **2**-Na in quantitative yield (eq 6). The identity of **2**-Na was proven both

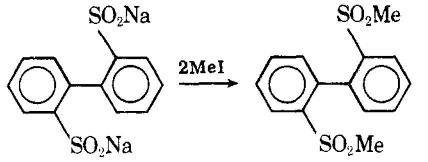


12 5-Na (5)



3 2-Na (6)

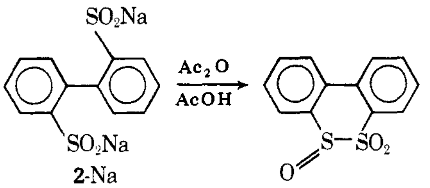
by its spectral properties and by its alkylation with methyl iodide to give the dimethyl sulfone **13** (eq 7). It was also further



13 (7)

substantiated by the conversion of **2**-Na to sulfinyl sulfone **11** discussed below.

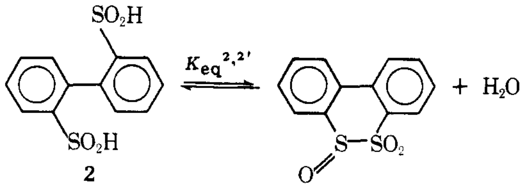
Disodium diphenyl-2,2′-disulfinate (**2**-Na) was treated with a mixture of equal volumes of glacial acetic acid and acetic anhydride. After removal of the excess acetic acid and anhydride the residue was extracted with chloroform to separate the sulfinyl sulfone from the sodium acetate that had also been formed. Workup of the chloroform extract yielded the cyclic sulfinyl sulfone **11**, dibenzo[*c*,*e*]-1,2-dithiin 1,1,2-trioxide, in 65% yield (eq 8). All spectral and analytical data were in accord



2-Na 11 (8)

with those expected for **11**. The cyclic sulfinyl sulfone has a long-wavelength absorption maximum at 310 nm (ϵ 5400) that can be used very conveniently to detect its presence in dilute solutions and also to distinguish it easily from cyclic thiolsulfonate **3**.

The Diphenyl-2,2′-disulfinic Acid–11 Equilibrium. As noted earlier, Kice and Margolis[3] found that acidification of a dilute (10^{-4} M) 60% dioxane solution of **5**-Na resulted in a mixture of **5** and **6** (eq 4) in which 75% of the material was present as the sulfinyl sulfone **6**. In contrast, acidification of a 10^{-4} M solution of disodium diphenyl-2,2′-disulfinate (**2**-Na) in 60% dioxane led to a situation where no significant fraction of the material was present as sulfinyl sulfone **11**. Clearly, then, the equilibrium constant for the equilibrium between **2** and **11** (eq 9) is much smaller than $K_{eq}^{1,8}$ for the equilibrium between **5** and **6**.



2 11 (9)

$$K_{eq}^{2,2'} = [11]/[2]$$

One should also note that we found *no* evidence that **2** alone upon standing in acidic aqueous dioxane forms any significant amount of cyclic thiolsulfonate **3**.

Although K_{eq} for the **2**–**11** equilibrium (eq 9) is much smaller than that for the **5**–**6** equilibrium (eq 4), experiments in acetic acid–water solvent demonstrate that it is at the same time *much larger* than K_{eq} for the equilibrium between an ordinary aromatic monosulfinic acid and its sulfinyl sulfone shown in eq 3.

When **2**-Na (10^{-4} M) was dissolved in acetic acid–5% water–0.10 M H_2SO_4 the absorbance of the solution at 310 nm increased from an initial value of 0.03 and finally leveled off at an equilibrium value of 0.33, owing to the conversion of **2** to an equilibrium mixture of **2** and **11** where the ratio [**11**]/[**2**] = 1.4 ± 0.2. The same value for $([\mathbf{11}]/[\mathbf{2}])_{equil}$ was also obtained by dissolving a sample of **11** (10^{-4} M) in the same solvent and observing the decrease in absorbance at 310 nm until it leveled off at a final constant value.

From earlier studies[4] one can estimate[5] that for the equilibrium in eq 3 (Ar = Ph), $K_{eq} = [PhS(O)SO_2Ph]/[PhSO_2H]^2 = 0.0023$ in acetic acid–5% water–0.10 M H_2SO_4. This means that K_{eq} for the **2**–**11** equilibrium (1.4 ± 0.2) is about 600 times larger than the equilibrium constant for sulfinyl sulfone formation from benzenesulfinic acid. A single experiment in acetic acid–1% water–0.10 M H_2SO_4 which indicated $([\mathbf{11}]/[\mathbf{2}])_{equil} \cong 8$ in that medium, as compared with $[PhS(O)SO_2Ph]/[PhSO_2H]^2 = 0.0133$ previously measured[4b] for $PhSO_2H$ under the same conditions, suggests that generally K_{eq} for the **2**–**11** equilibrium is about 600 times larger than that for the $PhSO_2H$–$PhS(O)SO_2Ph$ equilibrium.

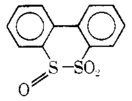
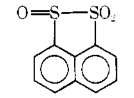
Rate of Spontaneous Hydrolysis of Sulfinyl Sulfone 11. The rate of spontaneous hydrolysis of **11** in 60% dioxane can be conveniently monitored by observing the decrease in absorbance at 310 nm and follows excellent first-order kinetics. The results are shown in Table I together with data on the rates of spontaneous hydrolysis of phenyl benzenesulfinyl sulfone and cyclic sulfinyl sulfone **6** in the same solvent.[3,6] One sees that the rates of hydrolysis of the three sulfinyl sulfones differ by only a factor of 20, the open-chain compound hydrolyzing about ten times faster than **11**, while the latter hydrolyses about twice as fast as the 1,8-naphthalene derivative **6**.

These results show that the large differences in K_{eq} for sulfinyl sulfone formation among the different compounds are only in modest measure due to differences in the rates of hydrolysis of the different sulfinyl sulfones. The major factor is, as seems quite reasonable, differences in the rates of formation of the sulfinyl sulfone from the corresponding sulfinic acids.

Behavior of Disodium Diphenyl-2,2′-disulfinate upon Acidification in the Presence of Sulfite. A 60% dioxane solution of disodium diphenyl-2,2′-disulfinate (**2**-Na 10^{-4} M) and a 20-fold excess of sodium sulfite was allowed to stand for several hours at room temperature. There was no change in the UV spectrum of the solution, indicating that **2**-Na and sulfite do not react. The solution was then acidified with aqueous sulfuric acid until $[H^+] = 0.1$ M. A strong peak, previously shown by experiments involving sulfite alone to be due to H_2SO_3, appeared in the spectrum. To determine if any **3** or **11** had been formed, the H_2SO_3 was purged from the solution. Examination of the ultraviolet spectrum after the H_2SO_3 had been removed showed that no detectable amount of either **3** or **11** had been formed. The spectrum was the same as that observed previously when a dilute aqueous dioxane solution of **2**-Na alone was acidified. This shows conclusively that diphenyl-2,2′-disulfinic acid (**2**) itself does *not* react with either H_2SO_3 or HSO_3^- to give cyclic thiolsulfonate **3**.

At this point we began to wonder whether or not **2**-Na was in fact the product formed from disulfonyl chloride **1** upon sulfite reduction, since, at least in experiments in homogeneous solution, **2**-Na showed no tendency to go over upon acidification to thiolsulfonate **3**, either in the presence or absence of sulfite. Proof that **2**-Na is indeed the product of the reduction of **1** by sulfite was provided by the experiment described in the following paragraph.

Table I. Rates of Spontaneous Hydrolysis of Selected Sulfinyl Sulfones in 60% Aqueous Dioxane[a]

Compd	$k_{hyd} \times 10^3$, s^{-1}
$PhS(O)SO_2Ph$	16
	1.6
	0.7

[a] Data are for 25 °C.

Proof That Disodium Diphenyl-2,2′-disulfinate Is the Product of the Reduction of Diphenyl-2,2′-disulfonyl Chloride by Sulfite. A sample of disulfonyl chloride **1** was reduced with excess sulfite in the usual manner and a small portion of the final clear reaction solution was added to 100 times its volume of anhydrous dioxane to make a solution 10^{-4} M in the reduction product of **1**. The excess sulfite could then be removed by filtration because sodium sulfite is quite insoluble in anhydrous dioxane. That the reduction product was the disulfinate **2**-Na was then demonstrated by treating the dilute solution of the reduction product in anhydrous dioxane with some acetic anhydride. This led to the immediate rapid development of the 310-nm peak in the ultraviolet spectrum of the solution associated with the formation of the cyclic sulfinyl sulfone **11**. The final intensity of the peak was approximately that expected if reduction of **1** by sulfite leads entirely to **2**-Na.

We had previously shown in a separate experiment that addition of the same amount of acetic anhydride to a dilute (1×10^{-4} M) solution of an authentic sample of disulfinate **2**-Na in anhydrous dioxane did in fact lead to the formation of the 310-nm peak associated with **11**.

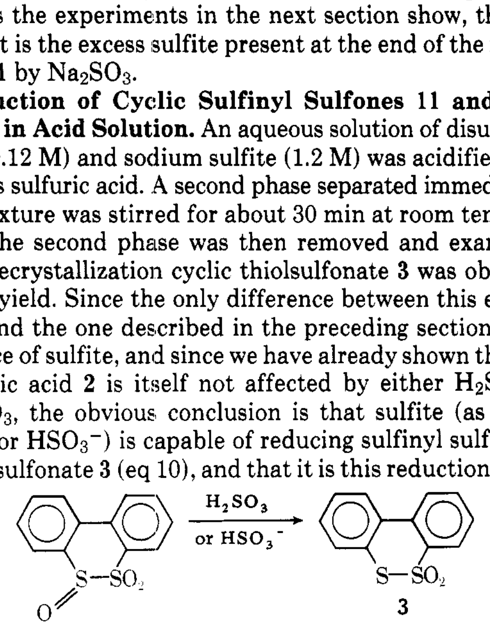
Thus, we can state with confidence that the reduction of disulfonyl chloride **1** by sulfite in weakly alkaline solution results in the formation of disulfinate **2**-Na. The problem now is to explain why acidification of the final reaction mixture from this reduction (a concentrated aqueous solution of **2**-Na plus excess sodium sulfite) leads to **3**, when acidification of **2**-Na in a dilute aqueous dioxane solution, either in the presence or absence of sulfite, does not.

Acidification of a Concentrated Aqueous Solution of Disodium Diphenyl-2,2′-disulfinate. Acidification of a relatively concentrated (0.1 M) *aqueous* solution of disulfinate **2**-Na led to the immediate separation of a second phase, presumably *initially* disulfinic acid **2**. This second phase was extracted using chloroform, and the extract dried. Addition of hexane to the chloroform solution led to the separation in 60% yield of material shown by spectral examination to consist of a mixture of disulfinic acid **2** and sulfinyl sulfone **11**, in which the latter predominated. Equally important, a TLC on the chloroform extract prior to the addition of hexane showed that it contained *no detectable amount* of cyclic thiolsulfonate **3**.

Thus, in marked contrast to the situation in aqueous dioxane, in the second, "sulfinic acid" phase which separates on acidification of a *purely* aqueous solution of **2**-Na there is present at equilibrium along with disulfinic acid **2** a significant amount of the cyclic sulfinyl sulfone **11**. The [**11**]/[**2**] ratio at equilibrium in this phase is thus akin to the type of situation found in acetic acid–5% water, and very different from that in media of much higher water content such as aqueous dioxane.

However, the lack of formation of any cyclic thiolsulfonate **3** under these conditions, even though a substantial fraction of the disulfinic acid is present as **11**, shows that one other ingredient is necessary before **3** can be formed at a significant rate. As the experiments in the next section show, that ingredient is the excess sulfite present at the end of the reduction of **1** by Na_2SO_3.

Reduction of Cyclic Sulfinyl Sulfones 11 and 6 by Sulfite in Acid Solution. An aqueous solution of disulfinate **2**-Na (0.12 M) and sodium sulfite (1.2 M) was acidified with aqueous sulfuric acid. A second phase separated immediately. The mixture was stirred for about 30 min at room temperature. The second phase was then removed and examined. Upon recrystallization cyclic thiolsulfonate **3** was obtained in 88% yield. Since the only difference between this experiment and the one described in the preceding section is the presence of sulfite, and since we have already shown that the disulfinic acid **2** is itself not affected by either H_2SO_3 or $NaHSO_3$, the obvious conclusion is that sulfite (as either H_2SO_3 or HSO_3^-) is capable of reducing sulfinyl sulfone **11** to thiolsulfonate **3** (eq 10), and that it is this reduction which is the final key step in the formation of **3** upon the reduction of **1** with excess sulfite and subsequent acidification of the reaction solution.

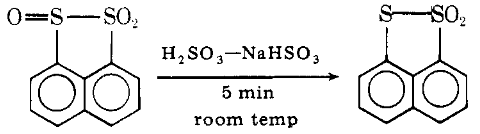


(10)

11

3

The relatively rapid spontaneous hydrolysis of **11** to **2** in aqueous dioxane makes it inconvenient to explore the proposed reaction shown in eq 10 in homogeneous aqueous dioxane medium. However, with cyclic sulfinyl sulfone **6** hydrolysis of the sulfinyl sulfone in acidic aqueous dioxane is not a problem, since, as noted earlier, **6** is strongly favored at equilibrium over its hydrolysis product, disulfinic acid **5**. Using **6** as the substrate one can therefore easily explore in a homogeneous solution whether a sulfinyl sulfone can in fact be readily reduced to the corresponding thiolsulfonate by an acidified solution of sodium sulfite in aqueous dioxane.



(11)

6

12

81%

Treatment of a solution of sulfinyl sulfone **6** (0.020 M) in acidic ($[H^+] = 0.1$ M) 60% dioxane with a solution of H_2SO_3 and $NaHSO_3$ ([total sulfite] = 0.5 M) in the same solvent, after 5 min at room temperature, gave upon workup an 81% yield of the corresponding cyclic thiolsulfonate **12** (eq 11). This experiment demonstrates unambiguously that a sulfinyl sulfone can be reduced easily to the corresponding thiolsulfonate by an acid solution containing sulfite. The existence of the reaction involving **11** and H_2SO_3 or $NaHSO_3$ shown in eq 10 would therefore seem to be proven beyond any reasonable doubt.

We do not as yet know anything definite about the mechanism of this reduction of sulfinyl sulfones by H_2SO_3 or $NaHSO_3$. Some speculative possibilities are discussed briefly in a footnote.[7]

Conclusions

The 50-year-old mystery[1] of the origin of the cyclic thiolsulfonate **3** formed upon reduction of diphenyl-2,2′-disulfonyl chloride (**1**) with sodium sulfite followed by acidification of the reaction solution has now been solved. The initial reduction of **1** by sulfite does indeed give disodium diphenyl-2,2′-disulfinate (**2**-Na), the expected, "normal" product of reduction of the disulfonyl chloride by sulfite. If acidification of the reaction mixture containing the disulfinate and excess sodium sulfite is carried out under conditions where both the disulfinic acid **2** formed on protonation of **2**-Na does not separate as a second phase, and also in a medium where the water concentration is high, then no **3** is formed, because the disulfinic acid **2** itself does not give **3**, either in the presence or absence of sulfite. On the other hand, the usual procedure of acidification of a concentrated aqueous solution of **2**-Na leads to the separation of disulfinic acid **2** as a second, separate phase, and in this second phase conditions are such that at equilibrium a substantial fraction of the disulfinic acid goes over to the cyclic sulfinyl sulfone **11** (eq 9). The excess sulfite left over from the original reduction of the disulfonyl chloride, and now present as a mixture of H_2SO_3 and $NaHSO_3$, then readily reduces sulfinyl sulfone **11** to thiolsulfonate **3** (eq 10).

Although unambigously established only for the transformation of disulfonyl chloride **1** to thiolsulfonate **3**, a similar sequence of events would seem almost certain to be involved in those other cases[2] in which sulfite reduction of an aromatic disulfonyl chloride has been reported to lead to a cyclic thiolsulfonate. Furthermore, one might well expect that analogous behavior, i.e., formation of cyclic thiolsulfonates, will be observed upon sulfite reduction of any disulfonyl chloride where the equilibrium constant for sulfinyl sulfone formation from the resulting disulfinic acid is large enough so that there will be a significant amount of the sulfinyl sulfone present at equilibrium. This sulfinyl sulfone will then undergo reduction by H_2SO_3 or HSO_3^- to the corresponding thiolsulfonate.

Experimental Section

General. *p*-Dioxane was purified according to the procedure of Hess and Frahm;[9] the freshly distilled dioxane was frozen and stored at −20 °C to prevent the formation of peroxides prior to use. Acetic acid was purified by a procedure described by Wiberg:[10] refluxing with acetic anhydride for 24 h followed by careful fractional distillation, only the middle third of the distillate, bp 115–116 °C, being retained. All water used in kinetic studies was doubly distilled from glass. The purity of the concentrated sulfuric acid used was determined by titration.

2-Iodobenzenesulfonic Acid (7). Commercial aniline-2-sulfonic acid (48 g, 0.25 mol) was dissolved in 300 mL of water and anhydrous sodium carbonate (14 g, 0.132 mol) was added with stirring until a homogeneous solution was obtained. Sodium nitrite (20 g, 0.28 mol) was then added to this solution and dissolved. After cooling to 0 °C the solution was added to 50 mL of concentrated hydrochloric acid plus 250 g of crushed ice. Immediate precipitation of the diazonium salt was observed. A solution of potassium iodide (50 g, 0.30 mol) in 50 mL of water was then added slowly with stirring. The mixture was allowed to warm slowly to room temperature and then heated to boiling to remove all nitrogen. Upon concentration of the solution crystalline **7** was obtained in 78% yield (55 g, 0.195 mol): mp 344–345 °C; IR (KBr) 3497 (m) and 1210 cm^{-1} (s).

2-Iodobenzenesulfonyl Chloride. Sulfonic acid **7** was neutralized by titration with sodium hydroxide solution in order to obtain sodium 2-iodobenzenesulfonate. This salt was dried in vacuo (0.1 Torr) at 150 °C for 3 h. Treatment of the sodium salt (10 g, 32.7 mmol) with phosphorus pentachloride (10 g, 48 mmol) at room temperature gave, after a few minutes, a liquid mixture with the generation of heat. After distilling off the phosphorus oxychloride that had been formed at reduced pressure, the sulfonyl chloride was collected by distillation at 135 °C (1 Torr). It was recrystallized from chloroform and hexane to give 8.0 g (80%) of 2-iodobenzenesulfonyl chloride: mp 51.5–52.5 °C; IR (KBr) $>SO_2$ group absorptions at 1362 (s) and 1178 cm^{-1} (s); mass spectral peaks at 60 °C and 20 eV (intensity), *m/e* 304 (M^+, 18.2), 302 (M^+, 53.5), 267 ($M^+ - Cl$, 44.1), 203 ($M^+ - SO_2Cl$, 100), 127 (I, 17.9), 113 (10.7), 111 (31.9), and 76 (C_6H_4, 96.4).

Phenyl 2-Iodobenzenesulfonate (8). 2-Iodobenzenesulfonyl chloride (4.4 g, 14.5 mmol) was mixed with phenol (2.8 g, 29.8 mmol) and anhydrous sodium carbonate (2.4 g, 22.6 mmol) at room temperature. After heating to 120 °C for 1.5 h, the excess phenol was distilled off at reduced pressure, and the residue was crystallized from chloroform and hexane. Compound **8** was obtained in 96% yield (5.0

g, 13.9 mmol): mp 91.5–92.5 °C; IR (KBr) >SO_2 group absorptions at 1371 and 1198 cm^{-1}; mass spectral peaks at 60 °C and 20 eV (intensity), *m/e* 360 (M^+, 34.2), 267 ($M^+ - OC_6H_5$, 38.1), 203 ($M^+ - SO_2OC_6H_5$, 64.1), and 76 (C_6H_4, 35.0).

Diphenyl Diphenyl-2,2′-disulfonate (9). Compound 8 (25 g, 69.4 mmol) was mixed with 25 g of copper dust, and the mixture was heated to 195 °C for 17 h with occasional stirring. After cooling back to room temperature, the mixture was extracted with chloroform for 10 h in a Soxhlet extractor. Crystalline 9 was obtained from the chloroform extract upon addition of hexane in 78% yield (12.7 g, 54.1 mmol): mp 127–128 °C; IR (KBr) >SO_2 group absorptions at 1376 (s) and 1158 cm^{-1} (s). The mass spectrum of the compound (140 °C and 70 eV) does not show a molecular ion peak, the highest *m/e* peak observed being at 373 ($M^+ - OC_6H_5$). However, the conversion of 9 to disulfonyl chloride 10 and the analytical data on the disulfonyl chloride leave no doubt that 9 has the structure assigned to it.

Diphenyl-2,2′-disulfonyl Chloride (1). Compound 9 (29 g, 62.2 mmol) was suspended in 100 mL of *n*-butyl alcohol, and a solution of sodium *n*-butoxide, prepared by dissolving 5 g (0.22 g-atom) of sodium metal in 250 mL of *n*-butyl alcohol, was added. The mixture was heated under reflux for 14 h. At the end of this time 300 mL of *n*-butyl alcohol was distilled off and the residue was added to 250 mL of water. After filtering, the solution was acidified with concentrated hydrochloric acid to pH 1. It was then extracted three times with 100-mL portions of ether in order to remove phenol. The acidic aqueous solution was then neutralized with 10% sodium hydroxide to pH 7 and evaporated to dryness. Without further purification the crude disodium diphenyl-2,2′-disulfonate was dried in vacuo (0.1 Torr) at 150 °C for 8 h. The crude powdered salt was then treated with 26 g (0.125 mol) of phosphorus pentachloride. This resulted in the generation of heat and the formation of a thick slurry. After distilling off the phosphorus oxychloride that had been formed under water pump vacuum, the solid residue was dissolved by treating it with a mixture of chloroform and 10% aqueous sodium carbonate. The chloroform layer was removed, filtered, and the filtrate dried over magnesium sulfate. Crystalline 1 was obtained from the chloroform solution upon addition of hexane in 78% yield (17.0 g): mp 144–145 °C; IR (KBr) SO_2 group absorptions at 1371 (s) and 1179 cm^{-1} (s). Anal. Calcd for $C_{12}H_8S_2O_4Cl_2$: C, 41.04; H, 2.30; Cl, 20.19. Found: C, 40.98; H. 2.19; Cl, 20.08. Compound 1, like diester 9, does not show a molecular ion peak in its mass spectrum (150 °C, 20 eV). The highest *m/e* peak observed is at *m/e* 315 ($M^+ - Cl$) and the strongest peak is at *m/e* 251 ($M^+ - SO_2Cl$). However, the elemental analysis data above leave no doubt that the compound is in fact the disulfonyl chloride 1, even though its melting point is a few degrees higher than that previously reported for 1 by Barber and Smiles.[1]

Dibenzo[*c,e*]-1,2-dithiin 1,1-Dioxide (3). Disulfonyl chloride 1 (11.4 g, 32.6 mmol) was suspended in 400 mL of 30% sodium sulfite solution (25-fold excess), and 45 mL of 10% NaOH was added. After heating under reflux for 1 h a clear, colorless solution was obtained. This was filtered and then acidified slowly by addition of concentrated sulfuric acid in the cold until the pH of the solution was <1.0. The resulting white cloudy mixture was heated slowly with stirring until the supernatant liquid was clear again. The white precipitate which had separated was collected and recrystallized from chloroform–hexane to afford 7.4 g (93%) of cyclic thiolsulfonate 3: mp 132–133 °C; IR (KBr) SO_2 absorptions at 1310 (s), 1161 (m), and 1123 cm^{-1} (s); UV (60% dioxane) λ_{max} 296 (ϵ 8660) and 262 nm (ϵ 9330); mass spectral peaks at 75 °C and 70 eV (intensity), *m/e* 248 (M^+, 42.3), 184 ($M^+ - SO_2$, 100), 152 ($M^+ - S_2O_2$, 16.1), and 139 (42.9). Anal. Calcd for $C_{12}H_8S_2O_2$: C, 58.04; H, 3.25; S 25.82. Found: C, 57.95; H, 3.16; S, 25.91.

Disodium Diphenyl-2,2′-disulfinate (2-Na). Cyclic thiolsulfonate 3 (2.5 g, 10 mmol) was dissolved in 30 mL of pure dioxane, and a mixture of 1.14 mL of 30% hydrogen peroxide and 20 mL of 1 N NaOH solution was added to the dioxane solution of 3 with stirring. Reaction appeared to be immediate. The solvents were removed by evaporation under reduced pressure, with the final traces of solvent being removed by heating the sample at 50 °C for 12 h under 0.05-Torr pressure. The salt was obtained in quantitative yield: mp 145–146 °C dec; IR (KBr) 1016 (s) and 958 cm^{-1} (s). Positive identification of the structure of 2-Na was provided by its conversion to (a) dimethyl diphenyl-2,2′-disulfone and (b) dibenzo[*c,e*]-1,2-dithiin 1,1,2-trioxide in the experiments described in the next two paragraphs.

Dimethyl Diphenyl-2,2′-disulfone (13). Treatment of disulfinate 2-Na (1.3 g, 4.0 mmol) in 25 mL of pure methanol with methyl iodide (2 mL, 32.1 mmol) under reflux for 5 h gave a brownish solution. After removing all the solvent, the brownish residue was dissolved in 25 mL of chloroform and the chloroform solution extracted once with 10% sodium sulfite to remove traces of iodine. The chloroform layer was concentrated and then chromatographed through a column of silica gel (150 g) using benzene as eluent. The fractions containing disulfone 13 were combined and evaporated to dryness. An NMR spectrum and integral of the crude oily residue (1.3 g) showed that the disulfone was about 90% pure. After standing at room temperature for 2 days the disulfone finally began to crystallize. The first crop of crystals was recrystallized from chloroform–ethanol to give analytically pure 13 (0.3 g, 24%): mp 161–162 °C; IR (KBr) SO_2 absorptions at 1304 (s) and 1142 cm^{-1} (s); NMR ($CDCl_3$) δ 2.97 (s, 3, CH_3), 7.35–7.84 (m, 3), and 8.12–8.35 (m, 1). Anal. Calcd for $C_{14}H_{14}S_2O_4$: C, 54.42; H, 4.55; S, 20.62. Found: C, 54.29; H, 4.40; S, 20.78.

Dibenzo[*c,e*]-1,2-dithiin 1,1,2-Trioxide (11). A sample of disulfinate 2-Na (0.76 g, 2.33 mmol) was treated with 5 mL of hot glacial acetic acid and 3 mL of acetic anhydride for 15 min. A clear solution resulted. After removing all the solvent in vacuo, the residue was extracted three times with 10-mL portions of hot chloroform. Crystalline sulfinyl sulfone 11 was obtained upon addition of hexane to the concentrated chloroform extracts in 65% yield (0.40 g, 1.51 mmol): mp 146–147 °C (dec); IR (KBr) 1320 (s), 1149 (s), and 1066 cm^{-1} (ms); UV (acetic acid) λ_{max} 310 nm (ϵ 5400). Anal. Calcd for $C_{12}H_8S_2O_3$: C, 54.55; H, 3.05; S, 24.22. Found: C, 54.66; H, 3.10; S, 24.02.

Disodium Naphthalene-1,8-disulfinate (5-Na). Cyclic thiolsulfonate 12 (1.11 g, 5 mmol), prepared by the method of Zweig and Hoffman,[11] was dissolved in 30 mL of anhydrous dioxane, and a solution of 0.67 mL of 30% hydrogen peroxide (5 mmol) and sodium hydroxide (0.40 g, 10 mmol) in 20 mL of water was added all at once with stirring. The resulting solution was evaporated to dryness and disulfinate 5-Na was obtained in quantitative yield: IR (KBr) 1033 (s), 980 (s), and 910 cm^{-1} (s); UV (dioxane) λ_{max} 295 nm (ϵ 7100). This procedure used for the preparation of 5-Na is a modification of the one originally used by Margolis[12] for the preparation of 5-Na. It appears to be somewhat superior and to give a somewhat purer product.

Naphtho[1,8-*cd*]-1,2-dithiole 1,1,2-Trioxide (6). A solution of 0.80 g (2.66 mmol) of disulfinate 5-Na in 10 mL of water was acidified with sulfuric acid to pH <1. The brownish precipitate of crude 6 was filtered off. Recrystallization of the crude material from chloroform–hexane gave pure cyclic sulfinyl sulfone 6 in 71% yield (0.45 g, 1.89 mmol): mp 168–169 °C; IR (KBr) 1330 (s), 1166 (s), 1136 (s), and 1081 cm^{-1} (s). Compound 6 was previously prepared by Margolis[3,12] by acidification of 5-Na in somewhat poorer yield and with a slightly lower melting point (160–162 °C). The infrared spectra of the two samples are identical, however.

Study of the Equilibrium between Diphenyl-2,2′-disulfinic Acid (2) and Cyclic Sulfinyl Sulfone 11. A stock solution of disodium diphenyl-2,2′-disulfinate (2-Na, 1.14×10^{-2} M) was prepared by dissolving 3.70 mg of 2-Na in 1.0 mL of water. The ultraviolet spectrum of 2-Na was recorded by transferring 32 μL of the stock solution through a microsyringe to a quartz, 1-cm UV cell containing 3.6 mL of 60% dioxane. The resulting concentration of 2-Na in the final solution was 1×10^{-4} M. After recording the spectrum of 2-Na, the solution in the cell was acidified by the addition of 60 μL of 12 N H_2SO_4; this makes the concentration of H^+ in the final solution 0.10 M. This acidification of the solution did not result in any significant change in the spectrum of the solution. In particular, even after allowing the solution to stand for 3 h, there was no significant increase in the absorbance of the solution at either 310 or 296 nm, such as would have been the case if significant amounts of either sulfinyl sulfone 11 or thiolsulfonate 3, respectively, were being formed from disulfinic acid 2 under these conditions.

In contrast, addition of 32 μL of the stock solution of the disulfinate 2-Na to 3.6 mL of acetic acid–5% water–0.10 M H_2SO_4 (prepared by the procedure outlined by Kice and Bowers[13]) led to an increase in the absorbance of the solution in the UV cell at 310 nm from an initial value of 0.03 to a final equilibrium value of 0.33, due to the formation from 2 of a significant amount of 11 at equilibrium. That the same value for the equilibrium ratio of [11]/[2] was obtained when the equilibrium was approached from the reverse direction was shown by an experiment in which 36 μL of a stock solution of sulfinyl sulfone 11 in acetic acid (prepared by dissolving 2.64 mg of 11 in 1.0 mL of acetic acid) was added to 3.6 mL of acetic acid–5% water–0.10 N H_2SO_4 and the absorbance of the solution at 310 nm was shown to decrease from an initial value of 0.53 to a final equilibrium value of 0.31. In another experiment 36 μL of the acetic acid stock solution of 11 was added to 3.6 mL of acetic acid–1% water–0.10 N H_2SO_4;[13] in this case the absorbance at 310 nm decreased from an initial value of 0.53 to a final equilibrium value of 0.48. All of the above experiments were carried out at 25 °C using a thermostated Cary 17 spectrophotometer.

Kinetics of the Spontaneous Hydrolysis of Sulfinyl Sulfone

11 in 60% Dioxane. The kinetics of the spontaneous hydrolysis of sulfinyl sulfone **11** in 60% dioxane were studied by adding 36 μL of a stock solution of **11** (1×10^{-2} M) in anhydrous dioxane to 3.6 mL of 60% dioxane containing 0.01 M $HClO_4$ and then monitoring the disappearance of the peak due to **11** at 310 nm with time, using a Cary Model 17 spectrophotometer with the cell holder thermostated at 25 °C.

Behavior of Disodium Diphenyl-2,2′-disulfinate (2-Na) Plus Sodium Sulfite in Aqueous Dioxane. A solution of sodium sulfite (2×10^{-3} M) in 60% aqueous dioxane was prepared by adding 7 μL of an aqueous sodium sulfite solution (1.01 M) to 3.6 mL of 60% dioxane in a 1-cm UV cell. Addition to this solution of 32 μL of a stock solution of **2**-Na (1.14×10^{-2} M) in water gave a solution 1.0×10^{-4} M in **2**-Na and 2×10^{-3} M in sulfite. The ultraviolet spectrum of this solution resembled that obtained in the same solvent for **2**-Na without sodium sulfite added. The spectrum remained unchanged over a period of observation of 3 h at 25 °C. The solution in the cell was then acidified by the addition of 60 μL of 12 N H_2SO_4, to give a final $[H^+] = 0.10$ M. The acidification of the solution led to the formation of a very intense peak at 275 nm due to the H_2SO_3 that was formed on protonation of the sulfite. In order to be able to examine the spectrum of the remaining materials in the solution, the H_2SO_3 was purged from the solution by passing a gentle stream of nitrogen through it for 3 h at room temperature. Examination of the ultraviolet spectrum of the solution at the end of that time showed that it was identical with that obtained upon acidification of **2**-Na in 60% dioxane in the absence of sulfite. In particular *no* absorption peaks at either 296 (thiolsulfonate **3**) or 310 nm (sulfinyl sulfone **11**) were observed.

Acidification of a Concentrated Aqueous Solution of Disodium Diphenyl-2,2′-disulfinate (2-Na). A 0.1 M solution of **2**-Na in water was prepared by dissolving 0.33 g of **2**-Na in 10 mL of water. This was acidified at room temperature with concentrated sulfuric acid until pH <1. A milky solution resulted. This was extracted three times with 10-mL portions of chloroform. The combined chloroform extracts were dried over magnesium sulfate and then concentrated. Addition of hexane to the concentrated extracts gave a white precipitate, 0.16 g, mp 139–140 °C dec. This was shown by infrared examination to consist of cyclic sulfinyl sulfone **11** admixed with some diphenyl-2,2′-disulfinic acid (**2**). Its ultraviolet spectrum showed the λ_{max} at 310 nm characteristic of **11**. A TLC (silica gel) on the chloroform concentrate before the addition of hexane showed no detectable amount of cyclic thiolsulfonate **3**.

Identity of the Product of the Reduction of Diphenyl-2,2′-disulfonyl Chloride (1) with Sulfite Ion. A sample of **1** was reduced with excess sodium sulfite in alkaline aqueous solution in the manner previously described. The amount of **1** and the volume of solution used were such that the final aqueous solution would be 0.075 M in the reduction product of **1**. Dilution of 5 μL of this solution with 3.6 mL of 60% dioxane gave an ultraviolet spectrum resembling that of authentic **2**-Na at the same concentration. This solution was then acidified by the addition of 60 μL of 12 N H_2SO_4. This led to the development of the intense peak at 276 nm associated with the presence of H_2SO_3. The H_2SO_3 was removed by passing a slow stream of nitrogen through the solution for 3 h at room temperature. The ultraviolet spectrum of the resulting solution was identical with that of an acidified solution of **2**-Na of similar concentration and showed no evidence for the presence of any **11** or **3**.

In a second experiment 5 μL of the aqueous solution of the reduction product of **1** was added to 3.6 mL of *anhydrous* dioxane. This led to the precipitation of the excess sulfite left over from the reduction. This was filtered off. Addition of acetic anhydride (36 μL) to the filtrate led to the rapid development of the absorption peak at 310 nm associated with the cyclic sulfinyl sulfone **11**. Its intensity was such as to suggest that essentially all of the reduction product of **1** must be **2**-Na.

Proof that treatment of **2**-Na with excess acetic anhydride in anhydrous dioxane leads to the formation of sulfinyl sulfone **11** had already been demonstrated by the following experiment. In this experiment 32 μL of an aqueous stock solution of **2**-Na (1.14×10^{-2} M) was added to 3.6 mL of anhydrous dioxane, and then 36 μL of acetic anhydride (0.38 mmol) was added. Examination of the ultraviolet absorption spectrum of the solution showed the rapid development of the absorption peak at 310 nm associated with **11**. This peak reached its full intensity in about 5 min. The final intensity corresponded to that expected for effectively quantitative conversion of **2**-Na to **11**.

Reduction of Cyclic Sulfinyl Sulfones 11 and 6 by Sulfite in Acid Solution. The reduction of cyclic sulfinyl sulfone **11** by sulfite in acid was demonstrated indirectly as follows. A sample of disulfinate **2**-Na (0.60 g, 1.82 mmol) and 2.30 g (18.2 mmol) of sodium sulfite were dissolved in 10 mL of water. No change in the ultraviolet absorption spectrum of the solution was observed even after standing at room temperature for 1 h. Addition of 12 N H_2SO_4 to the solution until the pH <1 caused the evolution of some sulfur dioxide and the separation of a second phase as a white cloudy suspension. After stirring the solution at room temperature for 30 min a clear supernatant was obtained. The white precipitate which had separated was collected and was recrystallized from chloroform–hexane to give 0.41 g (88%) of **3**, identical in all respects with the material obtained earlier upon sulfite reduction of disulfonyl chloride **1** followed by acidification and gentle warming (vide supra).

In the experiment with **6**, 0.24 g (1 mmol) of this cyclic sulfinyl sulfone was dissolved in 40 mL of 60% dioxane which had been acidified with 12 N H_2SO_4 to pH <1. Sodium sulfite (3.1 g, 25 mmol) dissolved in 10 mL of water was added slowly with stirring at room temperature. Sufficient sulfuric acid was present so that the pH of the final solution was approximately 1.0. After 5 min the dioxane was removed from the solution through rotary evaporation, and the suspension of organic solid which separated from the now completely aqueous solvent was filtered off and recrystallized from chloroform–hexane to give 0.18 g (81%) of cyclic thiolsulfonate **12**, mp 147–148 °C, identical in all respects with the authentic sample of the same thiolsulfonate prepared earlier (vide supra) by the procedure of Zweig and Hoffman.[11]

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Registry No.—**1**, 56527-83-4; **2**, 63059-22-3; **2**-Na, 63059-23-4; **3**, 25331-82-2; **5**-Na, 63059-24-5; **6**, 57821-65-5; **7**, 63059-25-6; **8**, 63059-26-7; **9**, 63059-27-8; **10**, 51131-89-6; **11**, 63059-28-9; **12**, 40227-43-8; **13**, 34226-76-1; aniline-2-sulfonic acid, 88-21-1; 2-iodobenzenesulfonyl chloride, 63059-29-0.

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(5) In ref 4a equilibrium constants for sulfinyl sulfone formation from *p*-toluenesulfinic acid were measured at a variety of sulfuric acid concentrations in acetic acid–5% water. While the equilibrium constant for sulfinyl sulfone formation from benzenesulfinic acid was only measured in this particular solvent at $[H_2SO_4] = 1.0$ M, that experiment and others in acetic acid–1% water at various sulfuric acid concentrations show that without exception K_{eq} for $PhSO_2H$ is 0.35 ± 0.05 K_{eq} for *p*-$CH_3C_6H_4SO_2H$. From this fact and the fact that K_{eq} for p-$CH_3C_6H_4SO_2H$ in acetic acid–5% water–0.10 M H_2SO_4 should be 0.0065, K_{eq} for benzenesulfinic acid in this solution is estimated to be 0.0023.

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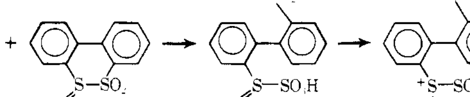
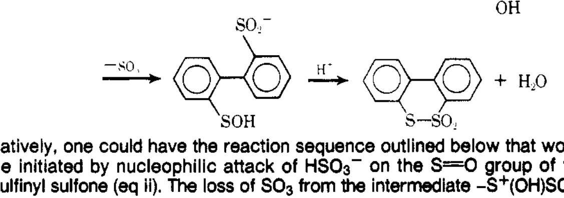
(7) Several possibilities for the mechanism of the reactions shown as eq 10 and 11 suggest themselves. First, one could have merely a simple oxygen transfer between the sulfinyl sulfone and H_2SO_3 (or HSO_3^-) (eq i). Alter-


(i)


(ii)

natively, one could have the reaction sequence outlined below that would be initiated by nucleophilic attack of HSO_3^- on the S=O group of the sulfinyl sulfone (eq ii). The loss of SO_3 from the intermediate $-S^+(OH)SO_3^-$ is reminiscent of the known breakdown of Bunte salts in acid solution,[8] $RS^+(H)SO_3^- \rightarrow RSH + SO_3$.

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