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Reactions of 1,2-Benzenedisulfinic Anhydride

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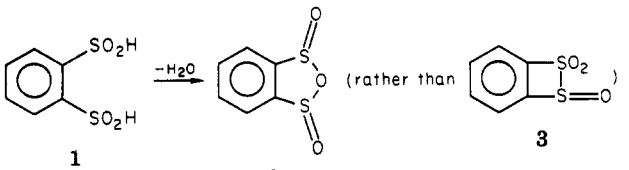
1,2-Benzenedisulfinic anhydride (2) is the first isolable example of an aromatic sulfinic anhydride. Its reaction with simple amines and alcohols is straightforward, the nucleophile (NuH) attacking one of the sulfinyl groups in 2 and forming the ring-opened substitution product, *o*-$NuS(O)C_6H_4SO_2H$ (4). However, when the nucleophile is either hydrazine or sulfite ion, the initial ring-opened substitution products undergo further reactions that lead in both cases primarily to the formation of the eight-membered cyclic bis(thiosulfonate), dibenzo-1,2,5,6-tetrathiocin 1,1,5,5-tetraoxide (8). Mechanisms for the formation of 8 are proposed. In contrast to acyclic aromatic sulfinyl sulfones, $ArS(O)SO_2Ar$, the cyclic sulfinic anhydride 2 is thermally quite stable, several weeks being required for its thermal decomposition at 55 °C. The principal product is 2,2′-dithiobis(benzenesulfonic acid), *o*-$HO_3SC_6H_4SSC_6H_4SO_3H$ (30).

The compound that Hendrickson et al.[1] believed was 1,2-benzenedisulfinic acid (1) has recently been shown[2] to be 1,2-benzenedisulfinic anhydride (2) the first isolable



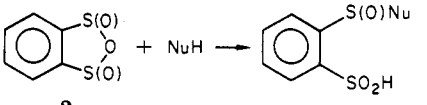
1 2 3

example of an aromatic sulfinic anhydride. Normally, "anhydride" formation from aromatic sulfinic acids ($ArSO_2H$) results in the formation of sulfinyl sulfones, $ArS(O)SO_2Ar$, rather than sulfinic anhydrides, $ArS(O)OS(O)Ar$.[3] The strain in the four-membered ring in sulfinyl sulfone 3 is thought[2] to be the reason that 2 is formed, instead of 3, upon loss of water from 1.

This paper reports the results of a study of the reactions of 2 with a group of different nucleophilic reagents and of its thermal decomposition.

Results and Discussion

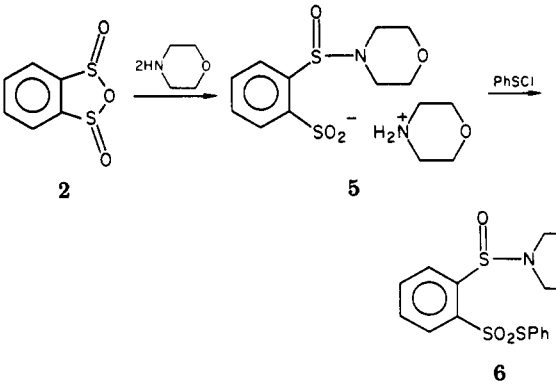
Reaction of 2 with Nucleophiles. Introduction. As might be anticipated from its rapid rate of hydrolysis,[2] 1,2-benzenedisulfinic anhydride (2) reacts extremely readily with common nucleophiles. We have examined its reaction with two nitrogen bases (morpholine and hydrazine), with two alcohols (methanol and ethanol), and with sulfite ion. The reactions with morpholine and with the two alcohols are straightforward and take the general course shown in eq 1. In the case of both hydrazine and



2 4 (1)

sulfite ion, however, the initial ring-opened substitution products are not stable and react further to produce somewhat unexpected products.

Reaction of 2 with Morpholine. Reaction of 2 with morpholine at 0 °C in acetonitrile is rapid and leads to the formation of the morpholinium salt of 2-(*N*-morpholinosulfinyl)benzenesulfinic acid (5).



2 5 6 (2)

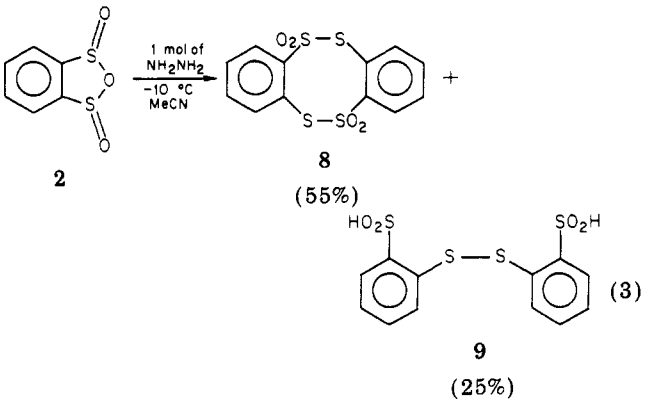
For analytical purposes 5 was converted by reaction with benzenesulfenyl chloride to thiosulfonate 6 (obtained in 93% yield from 2).

(1) Hendrickson, J. B.; Okano, S.; Bloom, R. K. *J. Org. Chem.* **1969**, *34*, 3434.
(2) Kice, J. L., Liao, S.-T. *J. Org. Chem.* **1981**, *46*, 2691.
(3) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65.

0022-3263/83/1948-2943$01.50/0

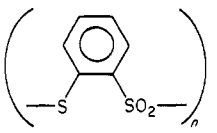
Reaction of 2 with Hydrazine. Reaction of hydrazine with **2** in the manner shown in eq 1 will yield a sulfinyl hydrazide (**4**, Nu = $NHNH_2$). These are known[4] to be extremely unstable and appear to decompose in the following manner: $-S(O)NHNH_2 \rightarrow -SOH + NH{=}NH$. In the present system this will result in the formation of 2-sulfenobenzenesulfinic acid, o-$HOSC_6H_4SO_2H$ (**7**), which, having a sulfenic acid group, will itself be unstable. Interest in just how **7** might react further was a major reason for examining the reaction of **2** with hydrazine.

Addition of 1 molar equiv of anhydrous hydrazine in acetonitrile to a solution of **2** at −10 °C results in an immediate reaction and the formation of two major products. The first, isolated in 55% yield, is the eight-membered cyclic bis(thiosulfonate), dibenzo-1,2,5,6-tetrathiocin 1,1,5,5-tetraoxide (**8**); the second, estimated (vide infra) to be formed in 25% yield, is 2,2′-dithiobis(benzenesulfinic acid), **9** (eq 3).



2 → **8** (55%) + **9** (25%) (3)

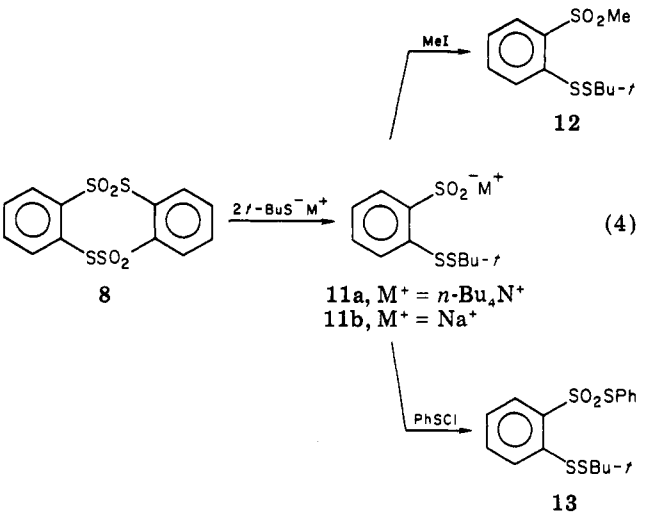
Cyclic bis(thiosulfonate) **8** is a high-melting compound that is insoluble in all common organic solvents except dimethylformamide and dimethyl sulfoxide and of very limited solubility even in these. We initially thought that the compound might be a low molecular weight polymer having structure **10**. However, since the mass spectrum



10

of the compound shows a quite strong (14%) molecular ion peak at m/e 344 and no evidence of any ions of higher mass, we have concluded that the substance is, in fact, **8**, rather than **10**.

The structure of **8** as a bis(thiosulfonate) was established both from its infrared spectrum (very strong, sharp bands at 1330 and 1147 cm^{-1}) and by several chemical transformations. Treatment of a suspension of **8** in methanol with 2 molar equiv of tetra-n-butylammonium 2-methyl-2-propanethiolate (n-Bu_4N^+t-BuS^-) led to the disappearance of **8** and the formation of a compound whose infrared and NMR spectra were consistent with its formulation as the tetra-n-butylammonium salt of 2-(*tert*-butyldithio)-benzenesulfinic acid (**11a**, eq 4). Confirmation of the structure of **11a** was provided by methylating the sulfinate group, using the procedure of Veenstra and Zwanenburg,[5] to give the methyl sulfone **12**, obtained in 90% yield. In another experiment, the sodium salt (**11b**), prepared by reacting a suspension of **8** with a solution of t-BuSNa, was



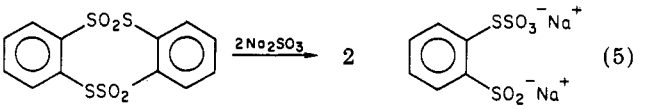
8 → **11a**, $M^+ = n$-Bu_4N^+; **11b**, $M^+ = Na^+$ (4)

12

13

treated with benzenesulfenyl chloride; S-phenyl 2-(*tert*-butyldithio)benzenethiosulfonate (**13**) was isolated in 70% yield.

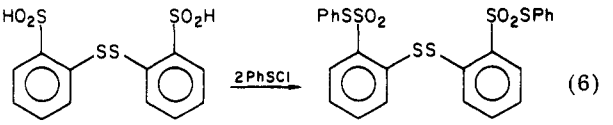
Stirring a suspension of **8** in an aqueous solution containing 2 molar equiv of sodium sulfite also led to the disappearance of **8**. Removal of the water from the resulting solution gave a quantitative yield of a product whose spectral properties were those expected for Bunte salt **14** (eq 5). Bunte salt **14** could be converted to **11b**



8 → **14** (5)

upon treatment with t-BuSNa.

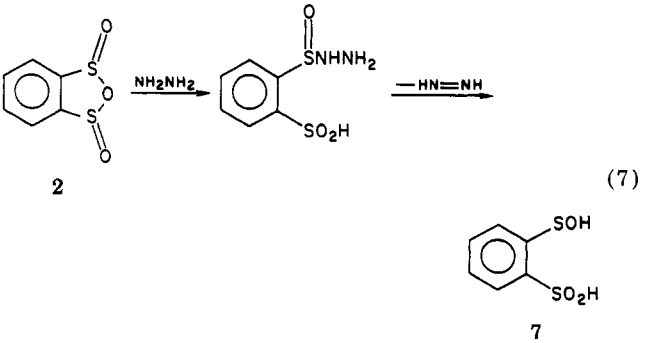
The structure and yield of **9** were established by reacting the two sulfinic acid groups in **9** with benzenesulfenyl chloride (eq 6) to form bis(thiosulfonate) **15**. On the basis



9 → **15** (6)

of the yield of **15**, the amount of **9** formed in the reaction of **2** with hydrazine is 25%.

As already outlined, reaction of hydrazine with **2** should give a sulfinyl hydrazide (**4**, Nu = $NHNH_2$) that immediately decomposes to **7** (eq 7). The task, then, is to

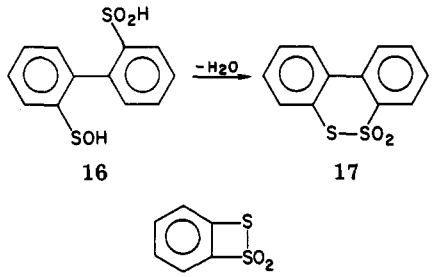


2 → **7** (7)

provide plausible pathways for the formation of **8** and **9** from **7**.

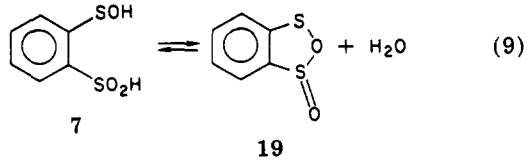
When formed as an intermediate, 2′-sulfenobiphenyl-2-sulfinic acid (**16**) gives the cyclic thiosulfonate dibenzo-[c,e]-1,2-dithiin 1,1-dioxide in essentially quantitative yield (eq 8).[6] An analogous intramolecular dehydration of **7** to

(4) Kobayashi, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2736.
(5) Veenstra, G. E.; Zwanenburg, B. *Synthesis* **1975**, 519.



16 17 18 (8)

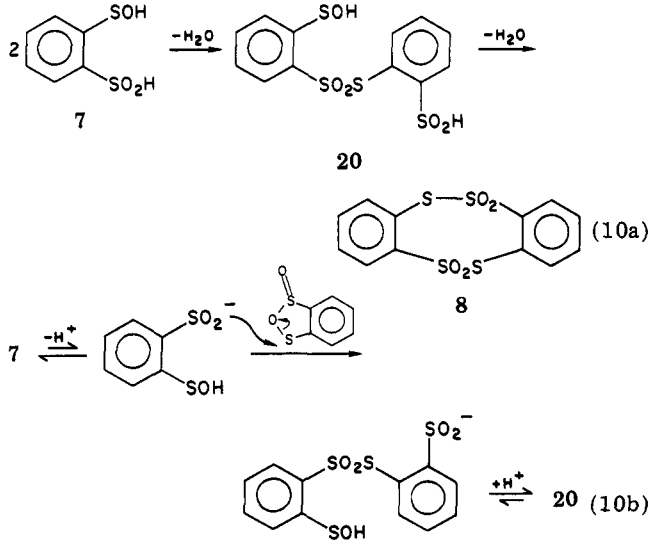
give **18** should be much less favorable, due to the strain that will be present in **18**. The fact that **2**, rather than **3**, is formed upon loss of water from **1**[2] suggests, however, that the alternative intramolecular dehydration of **7** to form the cyclic five-membered sulfenyl sulfinate (**19**), eq 9, might



7 19 (9)

be significant. Normally, sulfenyl sulfinates (RSOS(O)R) isomerize to the thermodynamically more stable thiosulfonate ($RSSO_2R$),[7] but the strain in **18** could easily be sufficient to make such an isomerization thermodynamically unfavorable. Our original hope, in undertaking the reaction of **2** with hydrazine, was that the dehydration in eq 9 would prove facile enough, and **19** stable enough, that **19** would be isolated as one of the principal final products of the reaction, thereby providing the first isolable example of a sulfenyl sulfinate. The fact that **19** is not found shows that the sulfenyl sulfinate is not stable enough to be isolated, even though isomerization to the thiosulfonate is disfavored. For this reason we show eq 9 as an equilibrium, rather than as a reaction where **7** is converted to **19**.

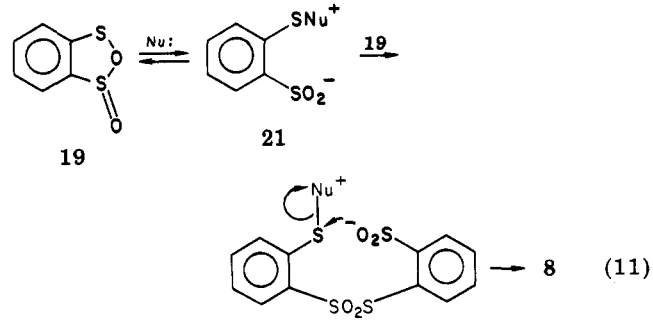
Intermolecular (rather than intramolecular) reaction of an –SOH and $-SO_2H$ group in **7** (eq 10a) will give **20**, which could then lose a second molecule of water intramolecularly to afford **8**; **20** would also result from nucleophilic attack of the $-SO_2^-$ group in the conjugate base of **7** on the dicoordinate sulfur of **19** (eq 10b). A third possible route to



7 20 8 (10a)

7 20 (10b)

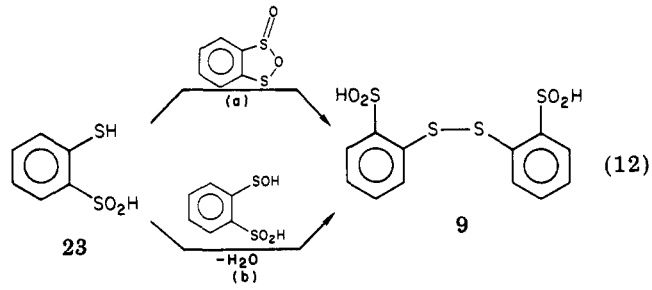
8 is the sequence shown in eq 11. Here some unspecified



19 21 22 8 (11)

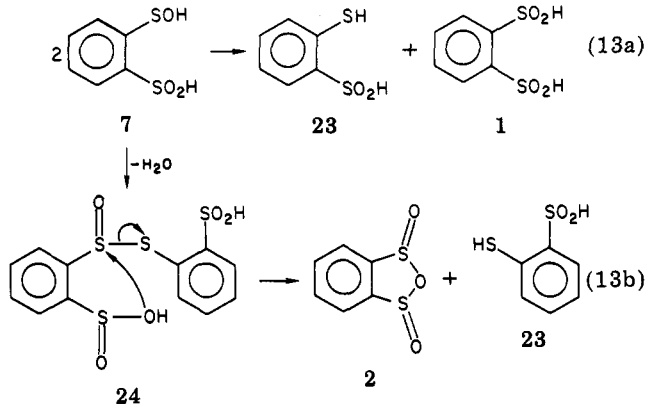
nucleophilic species (Nu:) reacts with **19** to form **21**. The $-SO_2^-$ group in **21** attacks the sulfenyl sulfur of a second molecule of **19** to form **22**, which then gives **8**.

Reaction of 2-mercaptobenzenesulfinic acid (**23**) with either **19** (eq 12a) or with the sulfenic acid group of **7** (eq 12b) appears to be the simplest way to account for the



23 9 (12)

formation of **9**. There are several reasonable routes by which **23** might be formed. One (eq 13a) is via disproportionation of the sulfenic acid groups in two molecules of **7**. A second (eq 13b) is the formation from **7** of thiosulfinate **24**, followed by an intramolecular nucleophilic substitution by one of the $-SO_2H$ groups at the sulfinyl group of **24**. A third, seemingly less likely route under



7 23 1 (13a)

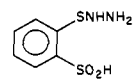
24 2 23 (13b)

the present conditions, is discussed in a footnote.[8]

The formation of both **8** and **9** from **7** can therefore be satisfactorily explained by a series of reactions (eq 9–13)

(6) Chau, M. M.; Kice, J. L. *J. Org. Chem.* **1977**, *42*, 3103.
(7) (a) Freeman, F.; Angeletakis, C. N.; Maricich, T. J. *J. Org. Chem.* **1982** *47*, 3403. (b) Freeman, F.; Angeletakis, C. N. *Ibid.* **1981**, *46*, 3391. (c) Chau, M. M.; Kice, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7711.

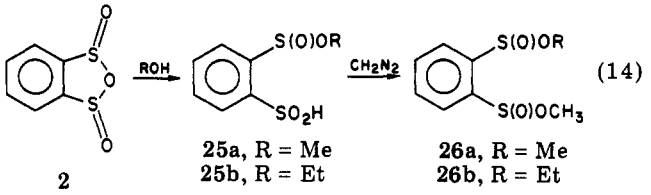
(8) A third route to **23** would be reaction of hydrazine with either **19** or **7** to give the sulfenyl hydrazide.



Sulfenyl hydrazides are known to decompose readily to thiol and diimide ($-SNHNH_2 \rightarrow -SH + HN{=}NH$).[9] Given the manner in which the reaction of **2** with hydrazine was carried out (gradual addition of a dilute solution of hydrazine to a solution of **2** over a 30-min period so that excess hydrazine was never present), formation of **23** by this route can only be significant if **19** is several orders of magnitude more reactive than **2** towards hydrazine.

all having reasonable precedent in sulfur chemistry.[9]

Reaction of 2 with Alcohols. Treatment with either methanol or ethanol converts **2** to the appropriate monoester (**25a** or **25b**) of 1,2-benzenedisulfinic acid. For isolation and characterization the $-SO_2H$ group of these monoesters was converted (eq 14) to an $-S(O)OCH_3$ group by methylation[10] with diazomethane, giving **26a** and **26b** in 100% yield based on **2**.



(14)

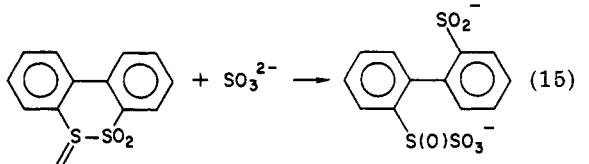
2

25a, R = Me
25b, R = Et

26a, R = Me
26b, R = Et

As isolated, **26a** is a mixture of the *dl* and meso stereoisomers. In contrast to the ^1H NMR for dimethyl naphthalene-1,8-disulfinate,[10] where the singlet for the CH_3O groups of the meso isomer occurs at slightly different (0.12 ppm) field than the singlet for the CH_3O groups in the other diastereomer, the singlets for the CH_3O groups in the two stereoisomers of **26a** occur at identical field. The ^1H NMR spectrum of **26b**, however, does show separate AB multiplets for the diastereotopic protons of the CH_2O groups in the erythro and threo diastereomers of that diester.

Reaction of 2 with Sulfite. Reaction of dibenzo[*c*,*e*]-1,2-dithiin 1,1,2-trioxide (**27**) with 1 molar equiv of sodium sulfite in aqueous dioxane gives the Bunte salt *S*-oxide (**28**) in excellent yield (eq 15).[6] For that reason



(15)

27 28

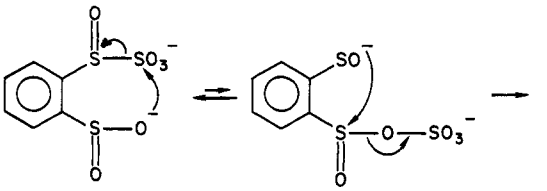
reaction of **2** with sulfite was anticipated to result in the formation of o-$^-O_2SC_6H_4S(O)SO_3^-$ (**29**). However, although **2** does react rapidly with sodium sulfite the product isolated is *not* **29**, but rather a mixture consisting of **8** (50%), **9** (~10%), sodium sulfate (50%), and 1,2-benzenedisulfinate (11%).

Given what was observed in the reaction of **2** with hydrazine, the formation of sizeable amounts of **8** (and some **9**) in the reaction of **2** with sulfite ion suggests the likelihood that **7** and/or **19** are formed as intermediates. The isolation of sodium sulfate indicates that sulfite ion is converted to SO_4^{2-}.

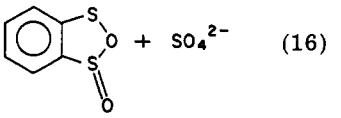
The Bunte salt *S*-oxide functionality in **28** decomposes rapidly in dilute acid solution in the following manner:[6]

$$-S(O)SO_3^- \xrightarrow{H^+} -SOH + SO_3 \xrightarrow{H_2O} H_2SO_4$$

An analogous decomposition for **29** would give **7** plus H_2SO_4. However, since it is unlikely that the present reaction solution ever becomes sufficiently acidic for acid-catalyzed decomposition of **29** to be important, some other route from **29** to either **7** or **19** appears needed. We tentatively suggest that sequence of intramolecular, nucleophilic displacements shown in eq 16; **19**, once formed, equilibrates with **7** (eq 9).[11]



29



(16)

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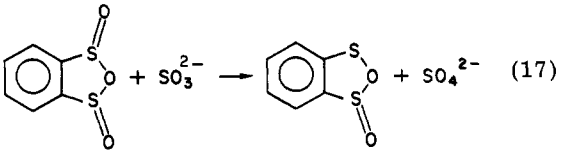
Alternatively, one could, of course, propose that SO_3^{2-} reacts with **2** via a direct transfer of one of the sulfinyl oxygens to the sulfite ion (eq 17). However, since reaction



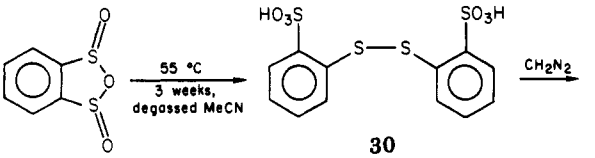
(17)

2 19

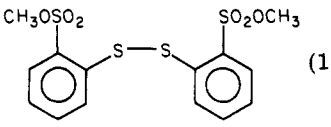
of sulfinyl sulfone **27** with sulfite takes place by nucleophilic attack of SO_3^{2-} on the sulfinyl sulfur, eq 17 seems a less attractive explanation for the results.

Thermal Decomposition of 2. When heated in anhydrous dioxane or acetonitrile acyclic aryl sulfinyl sulfones, $ArS(O)SO_2Ar$, undergo thermal decomposition very readily ($t_{1/2} \simeq 30$ min at 50 °C for Ar = *p*-tolyl).[12] Neither the nature of the solvent nor the aryl group has much effect on the rate.

In contrast to the thermal lability of $ArS(O)SO_2Ar$, cyclic sulfinic anhydride **2** is thermally very stable. Degassed solutions of **2** in acetonitrile had to be heated for several weeks at 55 °C to effect complete decomposition of **2** (eq 18). The principal final product was 2,2′-dithiobis(ben-



2 30



(18)

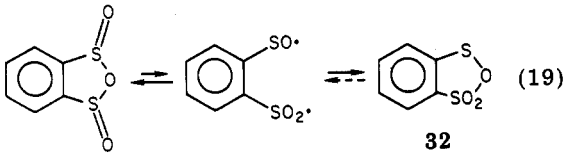
31

zenesulfonic acid), **30**, (90%); treatment of **30** with diazomethane converted it to the dimethyl ester (**31**), which was also characterized. Small amounts of **8** (5%) and 1,2-benzenedisulfonic acid (4%) were also formed in the thermal decomposition.

Thermal decomposition of acyclic aryl sulfinyl sulfones is known[12] to involve initial homolytic dissociation of the sulfur–sulfur bond, i.e., $ArS(O)SO_2Ar \rightarrow ArSO\cdot + ArSO_2\cdot$. Head-to-tail recombination of the radical pair results in

(9) Kice, J. L.; Rogers, T. E.; Warheit, A. C. *J. Am. Chem. Soc.* **1974**, *96*, 8020.
(10) Kice, J. L.; Krowicki, K. *J. Org. Chem.* **1981**, *46*, 4894.
(11) One may ask why a reaction sequence analogous to eq 16 was not observed[6] with **28**. A possible answer is that the ortho relationship of the reacting functional groups in **29** makes the reaction sequence a much more favorable one than for **28**, where the preferred conformation of the biphenyl system will place the reacting functional groups considerably further apart.
(12) Kice, J. L.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 4898.

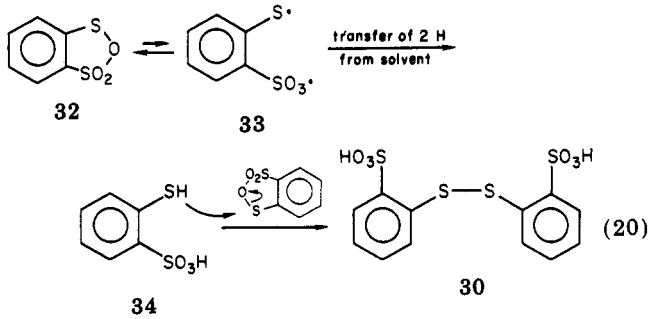
formation of the sulfenyl sulfonate, $ArSOSO_2Ar$. An analogous reaction sequence for **2** would lead to the formation of cyclic sulfenyl sulfonate **32** (eq 19).



(19)

2 **32**

Decomposition of an acyclic sulfenyl sulfonate ($ArSOSO_2Ar$, Ar = *p*-tolyl) under certain conditions has been shown[12] to give substantial amounts of *p*-tolyl disulfide (ArSSAr) and large amounts of *p*-toluenesulfonic acid ($ArSO_3H$). Decomposition of **32** to yield **30** therefore seems entirely possible. Several routes by which it might occur can be postulated. One (eq 20) would be via reversible homolysis of **32** to diradical **33**, abstraction of two hydrogen atoms from the solvent by **33**, and then rapid reaction of the *o*-mercaptobenzenesulfonic acid (**34**) so formed with another molecule of **32** in a nucleophilic substitution reaction to produce **30**.



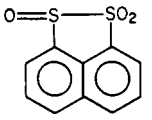
32 **33**

(20)

34 **30**

If the formation of **32** from **2** (eq 19) is reversible, with the equilibrium constant being such that the amount of **32** present at equilibrium is small, and if the vast majority of **33** formed from **32** recombines to regenerate **32**, rather than abstracting hydrogen atoms from the solvent to give **34**, this might offer an explanation for the very slow rate of thermal decomposition of **2** as compared with acyclic aryl sulfinyl sulfones.

Exploratory studies in this laboratory a number of years ago[13] indicated that the cyclic, five-membered aryl sulfinyl sulfone **35** was also extraordinarily stable thermally as compared to acyclic aryl sulfinyl sulfones. The current



35

finding that **2** is thermally much more stable than $ArS(O)SO_2Ar$ suggests that further investigation of the origin of the thermal stability of **35**, and of **2**, would be desirable.

Experimental Section

Preparation of 1,2-Benzenedisulfinic Anhydride (2). 1,2-Benzenedisulfonyl chloride[14] (6.5 g, 24 mmol) was added in small portions to a stirred solution of 6.4 g (50 mmol) of sodium sulfite and 8.3 g (99 mmol) of sodium bicarbonate in 65 mL of water kept at 40 °C. After the addition was complete the temperature was raised to 70–80 °C and stirring was continued for 1 h. The solution was then evaporated to dryness under reduced pressure, and the colorless, crystalline residue was dissolved in 60 mL of 30% sulfuric acid. After standing for 1 h at room temperature, this solution was extracted with twelve 50-mL portions of methylene chloride. The combined extracts were dried over calcium chloride, and the solvent was removed to give 3.5 g (79%) of **2**, which was recrystallized from approximately 45 mL of acetonitrile to yield 2.77 g (63%) of pure **2**: mp 135 °C dec; mass spectrum, *m/e* 188 (M^+, 34), 124 ($M^+ - SO_2$, 64), 96 (100), 70 (46), 50 (26), 39 (10), 28 (16). Anal. Calcd for $C_6H_4O_3S_2$: C, 38.29; H, 2.14. Found: C, 38.76; H, 2.27. The IR and NMR spectra of the material are the same as those previously reported[2] for **2**. The present method of workup and purification affords **2** in much greater yield and in higher purity (as judged by the higher melting point) than the procedures of either Kice and Liao[2] or Hendrickson et al.[1] An X-ray crystal structure shows that the compound isolated is the cis (meso) isomer of **2**.[15]

Reaction of 2 with Morpholine. Morpholine (0.120 g, 1.38 mmol) in 2 mL of acetonitrile was added at 0 °C to a stirred solution of 0.120 g (0.69 mmol) of **2** in 7 mL of the same solvent. After a few minutes benzenesulfenyl chloride[16] (0.10 g, 0.69 mmol) in 2 mL of acetonitrile was added. When the mixture had become colorless the solvent was removed under reduced pressure. The residue was dissolved in 50 mL of chloroform, the chloroform solution washed three times with 50 mL of water and dried ($CaCl_2$), and the chloroform removed under reduced pressure to afford 0.245 g (93%) of *S*-phenyl 2-(*N*-morpholinosulfinyl)-benzenethiosulfonate (**6**): mp 128–129 °C after recrystallization from chloroform–hexane; IR (KBr) 1445 (m), 1325 (s), 1145 (s), 1110 (s), 1080 (s), 910 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 8.4–7.0 (m, 9 H), 4.1–2.8 (m, 8 H). Anal. Calcd for $C_{16}H_{17}NO_4S_3$: C, 50.11; H, 4.47; N, 3.65. Found: C, 49.79; H, 4.60; N, 3.80.

Reaction of 2 with Hydrazine. Anhydrous hydrazine (0.35 mL, 11 mmol) in 30 mL of acetonitrile was added dropwise over a period of 30 min to a stirred solution of **2** (2.1 g, 11 mmol) in 200 mL of acetonitrile at −10 °C. The mixture was then allowed to warm to room temperature and filtered, and the precipitate was extracted six times with 15-mL portions of absolute ethanol. The ethanol extracts were combined with the acetonitrile filtrate.

The portion of the precipitate that did not dissolve in ethanol was pure dibenzo-1,2,5,6-tetrathiocin 1,1,5,5-tetraoxide (**8**), 1.05 g (55%). Recrystallization of **8** from dimethylformamide gave colorless needles that decompose at 265–270 °C without melting; IR (KBr) 1444 (m), 1421 (m), 1330 (vs), 1147 (vs), 1099 (m), 771 (m), 744 (m), 713 cm^{-1} (m); mass spectrum, *m/e* 344 (M^+, 14), 280 ($M^+ - SO_2$, 20), 216 ($M^+ - 2SO_2$, 100), 184 ($M^+ - 2SO_2 - S$, 82), 173 ($M^+/2$, 73). Anal. Calcd for $C_{12}H_8O_4S_4$: C, 41.84; H, 2.34; S, 37.26. Found: C, 42.03; H, 2.39; S, 37.06.

The combined ethanol–acetonitrile solution was evaporated under reduced pressure, leaving a yellowish, sticky residue (1.05 g). The IR spectrum of this residue has strong broad bands at 1030–1010 and 950 cm^{-1}. The residue was dissolved in 10 mL of dimethyl sulfoxide, 2 mL of methyl iodide was added, and the solution was allowed to stand overnight at room temperature. The reaction solution was added to 200 mL of methylene chloride, and the methylene chloride solution was washed first four times with 500 mL of water and then with aqueous sodium thiosulfate and dried over calcium chloride. The solvent was removed under reduced pressure and the residue was recrystallized twice from acetonitrile, giving 0.18 g of 2-(methylsulfonyl)phenyl disulfide: mp 220–222 °C; IR (KBr) 1440 (m), 1305 (s), 1150 (s), 1130 (m), 760 cm^{-1} (m); mass spectrum, *m/e* 374 (M^+, 100), 187 (74). Anal. Calcd for $C_{14}H_{14}O_4S_4$: C, 44.90; H, 3.77; S, 34.25. Found: C, 44.99; H, 3.87; S, 34.45.

In another experiment 1.92 mmol of **2** was reacted with an equimolar amount of hydrazine in the same fashion as described above. The final reaction mixture was evaporated to dryness under reduced pressure, and the residue was then extracted 3 times with 15-mL portions of hot water. (The water-insoluble portion of the residue, 0.166 g, was shown to be **8**.) The combined water extracts were evaporated under reduced pressure to ~15-mL total volume and were then passed through a column of

(13) Chau, M. M., unpublished results.
(14) Parham, W. E.; Roder, T. M.; Hasek, W. R. *J. Am. Chem. Soc.* **1953**, *75*, 1647.
(15) Hansen, H. C.; Hazell, R., Aarhus University, Denmark, unpublished results.
(16) Lecher, H.; Holschneider, F. *Ber.* **1924**, *57*, 755.

Dowex 50W-X8 ion exchange resin. The acidic eluate was treated with benzenesulfenyl chloride in ether by using the procedure of Stirling.[17] The ether phase was dried ($CaCl_2$) and evaporated. The residue (0.225 g) was chromatographed on silica gel with chloroform as eluent and yielded 0.135 g (25%) of *S,S'*-diphenyl 2,2'-dithiobis(benzenethiosulfonate), **15**: mp 158–159 °C after recrystallization from ether; IR (KBr) 1440 (m), 1327 (s), 1147 (s), 1126 (m), 748 (m), 594 cm^{-1} (s). Anal. Calcd for $C_{24}H_{18}O_4S_6$: C, 51.22; H, 3.22; S, 34.18. Found: C, 51.10; H, 3.36; S, 34.39.

Conversion of 8 to 12. A solution of 0.94 mmol of tetra-*n*-butylammonium 2-methyl-2-propanethiolate in methanol was prepared by mixing 0.94 mmol of 2-methyl-2-propanethiol (Aldrich) with an equimolar amount of tetra-*n*-butylammonium hydroxide in 10 mL of methanol. To this solution was then added 0.162 g (0.47 mmol) of **8**, and the suspension was stirred until all of **8** had dissolved and reacted (~2 h). Removal of the solvent gave tetra-*n*-butylammonium 2-(*tert*-butyldithio)benzenesulfinate (**11a**) as a colorless oil: IR (film) 3050 (s), 2950 (s, br), 2920 (s), 1465 (s, br), 1050–1020 (s, br), 975 cm^{-1} (s). Salt **11a** was then methylated with methyl iodide by using the procedure described by Veenstra and Zwanenburg.[5] 2-(*tert*-Butyldithio)phenyl methyl sulfone (**12**) was obtained as a slowly crystallizing oil (0.242 g, 93%): mp 74–75 °C after recrystallization from absolute ethanol; IR (KBr) ν_{SO_2} 1300 and 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.3–7.1 (m, 4 H) 3.25 (s, 3 H, CH_3SO_2) 1.34 (s, 9 H, $(CH_3)_3CS$); mass spectrum, *m/e* 276 (M^+, 7), 220 (M^+ – 56, 56), 141 (24), 57 (44), 28 (100). Anal. Calcd for $C_{11}H_{16}O_2S_3$: C, 47.79; H, 5.83; S, 34.80. Found: C, 47.70; H, 5.86; S, 34.06.

Conversion of 8 to 13. 2-Methyl-2-propanethiol (0.231 g, 2.6 mmol) was added to a solution of 0.102 g (2.6 mmol) of sodium hydroxide in 10 mL of absolute ethanol. This solution was then added to a stirred suspension of 0.440 g (1.3 mmol) of **8** in 20 mL of ethanol. The mixture was stirred until all of the **8** had dissolved and reacted. The solvent was then evaporated and the residue was dried under vacuum. Sodium 2-(*tert*-butyldithio)benzenesulfinate (**11b**) was obtained in quantitative yield; IR (KBr) 3000 (w), 1570 (w), 1430 (m), 1360 (m), 1048 (s), 1030 (s), 975 (s), 755 cm^{-1} (s).

Salt **11b** (0.385 g, 1.4 mmol) was dissolved in a mixture of 10 mL each of tetrahydrofuran and acetonitrile, and 0.20 g (1.4 mmol) of benzenesulfenyl chloride[16] was added with stirring. The color of the sulfenyl chloride disappeared and a precipitate formed. After 0.5 h 40 mL of methylene chloride was added. The mixture was then washed three times with 150 mL of water and dried ($CaCl_2$), and the solvents were removed to give *S*-phenyl 2-(*tert*-butyldithio)benzenethiosulfonate (**13**) as colorless crystals: 0.351 g (70%); mp 105–107 °C after recrystallization from ethanol; IR (KBr) ν_{SO_2} 1325 and 1135 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.4–7.0 (m, 9 H), 1.40 (s, 9 H); mass spectrum, *m/e* 370 (M^+, 10), 314 (M^+ – 56, 25), 281 (M^+ – 89, 25), 250 (13), 216 (7), 204 (31), 184 (21), 173 (29), 141 (46), 110 (100), 109 (17), 57 (100). Anal. Calcd for $C_{16}H_{18}O_2S_4$: C, 51.86; H, 4.90; S, 34.61. Found: C, 51.85; H, 4.89; S, 34.56.

Conversion of 8 to 14. Thiosulfonate **8** (0.125 g, 0.36 mmol) was added to a stirred solution of 0.091 g (0.72 mmol) of sodium sulfite in 2.5 mL of water kept at 40 °C. After ~2.5 h all of the **8** had dissolved and reacted. The water was then removed under reduced pressure and the residue was dried under vacuum in a desiccator. A quantitative yield of Bunte salt **14** was obtained: IR (KBr) 3610 (m), 3540 (m), 1615 (m), 1565 (m), 1240 (m), 1220 (s, $-SO_3^-$), 1045 (s, SO_2^-), 1030 (s, SO_2^-), 965 cm^{-1} (m, SO_2^-); discolors at 155 °C and envolves gas at 220 °C.

Bunte salt **14** (0.180 g, 0.58 mmol) was dissolved in 10 mL of methanol. To this was then added dropwise, with stirring, a solution of 0.58 mmol of tetra-*n*-butylammonium 2-methyl-2-propanethiolate in methanol (prepared as described earlier). The reaction mixture was stirred for 18 h, after which the solvent was evaporated and the residue dried. Methylation[5] of the residue with methyl iodide gave **12** in 92% yield.

Reaction of 2 with Methanol. 1,2-Benzenedisulfinic anhydride (0.098 g, 0.52 mmol) was dissolved in 3 mL of dry methanol and the solution allowed to stand at room temperature for 1 h. An excess of diazomethane in ether was then added to the stirred solution at 0 °C. Evaporation of the solvent under reduced pressure gave 0.124 g (100%) of a mixture of the meso and dl isomers of dimethyl 1,2-benzenedisulfinate (**26a**): mp 45–55 °C; IR (KBr) 2920 (w), 1440 (m), 1120 (s), 960 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 8.4–7.6 (m, 4 H), 3.64 (s, 6 H); mass spectrum, *m/e* 234 (M^+), 203 (M^+ – MeO), 188, 172, 124, 109, 96. Recrystallization from chloroform/hexane afforded one of the stereoisomers of **26a** in a pure state, mp 77–78 °C. Anal. Calcd for $C_8H_{10}O_4S_2$: C, 41.01; H, 4.30. Found: C, 40.85; H, 4.14.

Reaction of 2 with Ethanol. Anhydride **2** was reacted with ethanol, and the reaction product was treated with diazomethane in the same manner as in the reaction of **2** with methanol. Evaporation of the solvent gave 0.123 g (95%) of a mixture of the diastereomers of methyl ethyl 1,2-benzenedisulfinate (**26b**) as a colorless oil: IR (film) 2970 (m), 2930 (m), 1440 (m), 1140 (s), 1125 (s), 1010 (m), 960 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 8.3–7.6 (m, 4 H), 4.45–3.55 (pair of overlapping ABX_3 multiplets, 2 H) 3.57 (s, 3 H, CH_3O) 1.6–1.2 (m, 3 H, CH_3CH_2O).

Reaction of 2 with Sulfite Ion. A solution of 0.210 g (1.12 mmol) of **2** in 10 mL of acetonitrile was rapidly mixed with a solution of 1.12 mmol of sodium sulfite in 10 mL of water at room temperature. A few minutes after mixing the solution was frozen and the solvents were removed by lyophilization. The residue was then extracted three times with 15-mL portions of boiling water, followed by three extractions with 5-mL portions of boiling ethanol. The portion of the residue that did not dissolve, 0.097 g, was shown to be **8** (50% yield based on **2**).

The combined extracts were condensed to about 25 mL, acidified with 0.25 mL of 30% sulfuric acid, and then treated with benzenesulfenyl chloride in ether by using the procedure of Stirling.[17] The ether phase was dried and evaporated, and the residue was subjected to preparative TLC (silica gel/$CHCl_3$). There was obtained 0.036 g (0.06 mmol) of **15** and 0.052 g (0.12 mmol) of *S,S'*-diphenyl 1,2-benzenedithiosulfonate (**36**): mp 185–186 °C; IR (KBr) 1344 (m), 1329 (s), 1149 (s), 1124 (m), 754 cm^{-1} (s). Anal. Calcd for $C_{18}H_{14}O_4S_4$: C, 51.16; H, 3.34; S, 30.35. Found: C, 50.99; H, 3.38; S, 30.20. Thiosulfonate **36** was also synthesized independently by reaction of benzenesulfenyl chloride with 1,2-benzenedisulfinic acid (the latter prepared by the hydrolysis of **2**).

In another experiment, the residue after removal of the solvents was extracted first with ethanol and then with water. Evaporation of the aqueous extract gave, after drying in vacuo over P_2O_5, 0.080 g (0.56 mmol) of sodium sulfate; the IR spectrum was identical with that of a known sample.

Thermal Decomposition of 2. A solution of 0.234 g (1.24 mmol) of **2** in 15 mL of acetonitrile was placed in a 50-mL flask equipped with a stopcock, frozen, attached to a vacuum line, and degassed four times in the usual way. The degassed solution was then sealed and heated in an oil bath at 55 °C. After 3 weeks (preliminary experiments had shown that approximately this length of time was required for complete disappearance of **2**) the mixture was cooled to room temperature and opened, and a small amount (0.011 g) of a precipitate that had formed was filtered off. This was identified as **8**.

The acetonitrile was removed from the filtrate under reduced pressure, and the residue was extracted twice with 5-mL portions of distilled water. The combined aqueous extracts were passed through a column of Dowex 50W-X8 ion exchange resin. Removal of the water from the acidic eluate gave an oily residue. Treatment of the residue with 3 mL of dry methanol led to the crystallization of 0.04 g (0.11 mmol) of 2,2'-dithiobis(benzenesulfonic acid), **30**: mp >360 °C; IR (KBr) 1246 (s), 1221 (s), 1188 (m), 1132 (s), 1080 (w), 1057 (s), 1039 (w), 1012 (m), 771 (w), 756 (w), 700 (m), 615 (s), and 578 cm^{-1} (m). The methanol solution was treated with an excess of diazomethane in ether at room temperature. Removal of the solvents gave 0.17 g (0.42 mmol) of dimethyl 2,2'-dithiobis(benzenesulfonate), **31**: mp 110–111 °C, after recrystallization from chloroform/hexane; IR (KBr) 3094 (w), 3060 (w), 2662 (w), 2362 (w), 2341 (w), 1414 (s), 1359 (s), 1184 (s), 1035 (s), 981 (s), 791 (s), 758 (s), and 590 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 8.2–7.3 (m, 8 H), 3.85 (s, 6 H); mass spectrum, *m/e* 406 (M^+, 82), 203 ($M^+/2$, 100), 109 (55), 69 (20). Anal. Calcd for $C_{14}H_{14}O_6S_4$: C, 41.36; H, 3.47; S, 31.55. Found C, 41.26; H, 3.60; S, 30.59.

The residue (0.033 g) from the first water extractions could be dissolved in some additional water (~5 mL). Treatment of this

(17) Stirling, C. J. M. *J. Chem. Soc.* **1957**, 3597.