mixture was refluxed for 3 h, and this was recrystallized in water: yield 60%; ^{1}H NMR (Me_2SO-d_6) δ 7.65 (d, 1 H), 6.55 (m, 1 H), 3.25 (exchangeable by D_2O, NH), 2.05 (s, 3 H).

β-Substituted Succinaldehydic Acids. Method a: Catalytic Hydrogenation of 8. A solution of **8e** in ethyl acetate (3.5 g, 0.02 mol) was well stirred under 1 atm of hydrogen pressure with Pd as a catalyst (Engelhard, 10% Pd/C, 1 g of catalyst for 10 g of product). H_2 (1 equiv) was absorbed over a 3–4-h period. The catalyst suspension was removed by filtration. The organic layer was evaporated, and the residual oil was distilled at 190 °C under reduced pressure (0.05 mm) with a Kugelrohr distillation apparatus, giving 3 g of oil which crystallized: yield 86%; mp 77 °C; IR ($CHCl_3$) 3020 (Ph), 1780 (C=O lactone ring) 1715 cm^{-1} (C=O aldehyde); NMR ($CDCl_3$) δ 7.30 (m, 5 H), 5.9 (s, exchangeable with D_2O, OH), 3.25 (td, 1 H), 2.85 (d, 2 H).

Method b: Catalytic Hydrogenation of the γ-Ethoxybutanolides 11 and Hydrolysis. 4-Substituted 5-Ethoxy-4,5-dihydro-2(3*H*)-furanones (16). A solution of absolute ethanol containing **11** (0.05 mol in 100 mL) was hydrogenated under the same conditions as above. The residual oil was efficiently distilled under reduced pressure to give pure **16**. Purity of **16** was controlled by gas chromatography. All yields are better than 84%. Anal. Calcd for $C_7H_{12}O_3$ (**16a**): C, 58.31; H, 8.39. Found: C, 58.41; H, 8.30.

Hydrolysis of 16. Hydrolysis of **16a** (3 g, 0.021 mol) under the operating conditions described in the previous paper[1] afforded the crude oil after removal of the solvent. The distillation at 100 °C under reduced pressure (0.05 mm) with the same apparatus as above gave 2 g of a colorless oil: 66% yield; IR ($CHCl_3$) 3400 (OH), 1780 (C=O lactone), 1720 cm^{-1} (C=O aldehyde); NMR ($CDCl_3$) δ 6.45 (complex system, 2 H), 2.50 (m, 3 H), 1.1 (d, 3 H).

Registry No. **1d**·HCl, 78920-01-1; **2a**, 78920-02-2; **2b**, 78920-03-3; **2c**, 78920-04-4; **2d**, 78920-05-5; **2e**, 78920-06-6; **3a**, 78920-07-7; **3f**, 78939-67-0; **4**, 78920-08-8; **7**, 78920-09-9; **8a**, 40834-42-2; **8b**, 1575-49-1; **8c**, 78920-10-2; **8d**, 7755-27-3; **8e**, 78920-11-3; **9**, 78920-12-4; **10**, 78939-69-2; **11a**, 78920-13-5; **11b**, 78920-14-6; **11c**, 78920-15-7; **11d**, 78920-16-8; **11e**, 78920-17-9; **12**, 78920-18-0; **13d**, 78920-19-1; **14a**, 54709-94-3; **14d**, 78920-20-4; **14f**, 78920-21-5; **15b** (R = Ph), 78920-22-6; **15b** (R = Me), 61892-47-5; **16a**, 78920-23-7; **16b**, 78920-24-8; **16c**, 78920-25-9; **16d**, 78920-26-0; **16e**, 78920-27-1; **16f**, 78939-70-5; morpholine, 110-91-8; glyoxylic acid, 298-12-4; propanal, 123-38-6; butanal, 123-72-8; pentanal, 110-62-3; 3-methylbutanal, 590-86-3; benzenepropanal, 104-53-0; benzeneacetaldehyde, 122-78-1; morpholine hydrochloride, 10024-89-2; **11f**, 78920-28-2.

Reactions of Naphtho[1,8-*cd*]-1,2,3-trithiin 1,1,3,3-Tetraoxide (Naphthalene-1,8-disulfonothioic Acid Anhydrosulfide)

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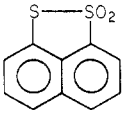
Received July 1, 1981

Attempts to oxidize naphtho[1,8-*cd*]-1,2,3-trithiin 1,1,3,3-tetraoxide (**5**) to the corresponding hexaoxide with oxidizing agents such as peracids, ozone, potassium permanganate, ruthenium tetraoxide, etc. were unsuccessful and led only to recovery of **5** unreacted. With the oxidizing agent HO_2^-, however, **5** reacts rapidly; the trithiin ring is cleaved and naphthalene-1-sulfinate-8-sulfonate (**6**) and naphthalene-1,8-disulfinate (**7**) are formed in approximately equal amounts. Opening of the trithiin ring in **5** also occurs readily upon treatment with triphenylphosphine or cyanide ion. With the phosphine an interesting sequence of further reactions follows the opening of the ring and results in the eventual formation of the unusual zwitterionic phosphonium salt **15**. This phosphonium salt undergoes thermal decomposition in boiling decalin to give triphenylphosphine oxide and cyclic thiosulfonate **1**. Alkaline hydrolysis of **5** occurs easily and gives disulfinate **7** plus some sulfite.

The most highly oxidized derivatives of trisulfides known to date are 1,1,3,3-tetraoxides RSO_2SSO_2R.[1] We wished, if possible, to prepare a more highly oxidized derivative, either a 1,1,2,3,3-pentaoxide [$RSO_2S(O)SO_2R$] or a 1,1,2,2,3,3-hexaoxide ($RSO_2SO_2SO_2R$), in order to ascertain its thermal stability and chemistry. Previous work[2] has suggested that oxidation of cyclic thiosulfonates **1** and **2** to the corresponding α-disulfones (1,1,2,2-tetraoxides)



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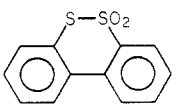

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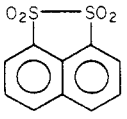

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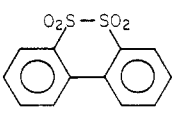
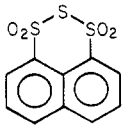


4

3 and **4** is considerably easier to achieve in good yield than oxidation of an acyclic aryl thiosulfonate to an α-disulfone. We felt therefore that the best chance to prepare a trisulfide hexaoxide would be to synthesize naphtho[1,8-*cd*]-1,2,3-trithiin 1,1,3,3-tetraoxide (naphthalene-1,8-disulfonothioic acid anhydrosulfide, **5**) and then to oxidize **5** with an oxidizing agent that would convert the central sulfur from >S to >SO_2.



5

As it turns out, none of the many oxidizing agents tried are effective; most simply lead to recovery of unreacted starting material, while one, HO_2^-, leads to cleavage of the sulfur-containing ring. Although oxidation of **5** to the corresponding 1,2,3-trithiin 1,1,2,2,3,3-hexaoxide has not been achieved, we have found that **5** undergoes some interesting reactions with various reagents that are described and discussed in the present paper. As in the chemistry

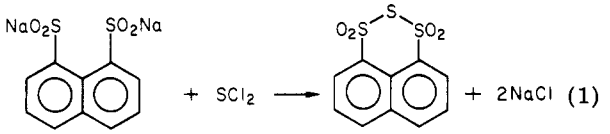
(1) Austad, T. *Acta Chem. Scand., Ser. A* **1955**, *A29*, 241.
(2) Chau, M. M.; Kice, J. L. *J. Org. Chem.* **1978**, *43*, 914.

0022-3263/81/1946-4894$01.25/0

of 1 and 2,[2] the close proximity of the various sulfur functionalities once the ring is opened can lead to rather facile further intramolecular reactions.

Results and Discussion

Naphtho[1,8-*cd*]-1,2,3-trithiin 1,1,3,3-tetraoxide (**5**) is easily synthesized by reacting sodium naphthalene-1,8-disulfinate[3] (**7**) with sulfur dichloride (eq 1).



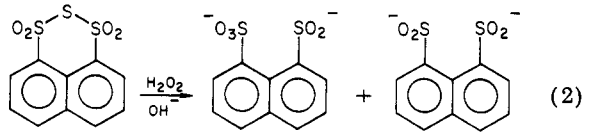
7 **5** (1)

Attempted Oxidation of 5. Oxidation of **5** was attempted by using a wide variety of oxidizing agents. Among those tried were *m*-chloroperbenzoic acid, peroxytrifluoroacetic acid, ozone, ruthenium tetraoxide, *tert*-butyl hypochlorite, triphenylphosphite ozonide, potassium permanganate (in the presence of 18-crown-6) in methylene chloride, bromine plus 1,4-diazabicyclo[2.2.2]-octane, sodium periodate, and $PhI(OAc)_2$. With the peracids, reaction times well in excess of those required[2] for the successful oxidation of **1** to **3** were employed, but no oxidation of **5** was observed. In view of the relatively easy oxidation of **1** to **3** by peracids, one can only conclude that the decrease in electron density on the dicoordinate sulfur induced by the presence of the second adjacent SO_2 group in **5** is clearly substantial and sufficient to render that atom no longer adequately reactive toward electrophilic oxidizing agents such as the peracids.

Treatment of **5** with 2 mol of ozone at -70 °C in methylene chloride and then allowing the solution to warm slowly to room temperature also does not lead to any detectable oxidation of **5** and neither does a similar treatment of **5** with triphenylphosphite ozonide. Allowing **5** to stand for several days with either *tert*-butyl hypochlorite, $PhI(OAc)_2$, or sodium periodate plus 18-crown-6 in chloroform at room temperature is also without effect. In the case of potassium permanganate or ruthenium tetraoxide, precipitates of MnO_2 and RuO_2, respectively, do slowly appear, but workup of the solutions leads to virtually complete recovery of **5**.

While the above oxidizing agents are without detectable effect on **5**, the same is not true for alkaline hydrogen peroxide.

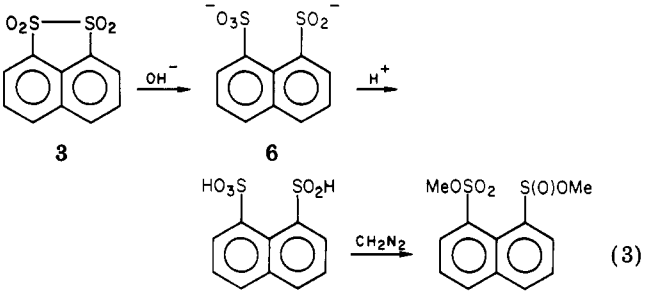
Reaction of 5 with Alkaline Hydrogen Peroxide. Reaction of **5** with hydrogen peroxide in alkaline solution is rapid and leads to the formation of a mixture of entirely water-soluble products. Infrared examination suggests that the organic components of this mixture are naphthalene-1-sulfinate-8-sulfonate (**6**) and naphthalene-1,8-disulfinate (**7**) (eq 2). Verification of this and an estimate of the



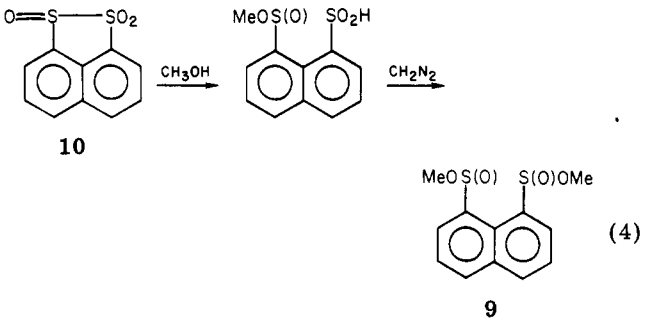
5 **6** (41%) **7** (49%) (2)

relative yields of **6** (41%) and **7** (49%) are achieved by conversion of the mixture of salts to the corresponding diacids, reaction of the diacids with diazomethane to give dimethyl naphthalene-1-sulfinate-8-sulfonate (**8**) and dimethyl naphthalene-1,8-disulfinate (**9**), and separation of esters **8** and **9** by chromatography.[4]

Authentic samples of **8** and **9** (which are both new compounds) were prepared by the routes shown in eq 3 and 4. Disulfinate **9** as isolated was shown by ^1H NMR



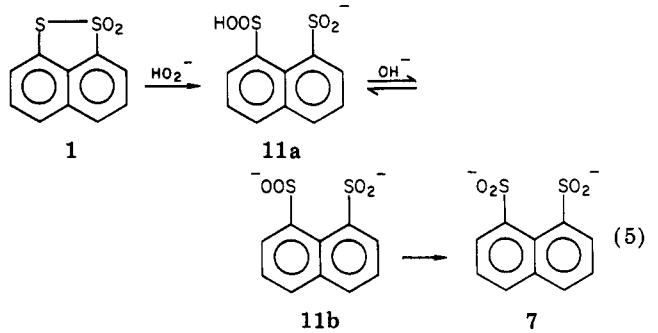
3 **6** **8** (3)



10 **9** (4)

(difference in δ for CH_3O groups) to be an 83:17 mixture of the *dl* and meso stereoisomers. The major diastereomer (thought to be the *dl*) can be easily separated by fractional crystallization. In methanol solution in the presence of a trace of methoxide it rapidly undergoes equilibration with the other diastereomer to give the 83:17 mixture mentioned above.

The dicoordinate sulfur atom in aryl thiosulfonates ($ArSO_2SAr$) is readily attacked by nucleophiles.[6] One might expect that the dicoordinate sulfur in **5** would also be easily attacked by nucleophiles, and the reactivity of **5** toward such nucleophilic reagents as CN^- and Ph_3P (vide infra) seems to bear this out. The course of the reaction of thiosulfonate **1** with HO_2^- is shown in eq 5.[2,6] It



1 **11a** **11b** **7** (5)

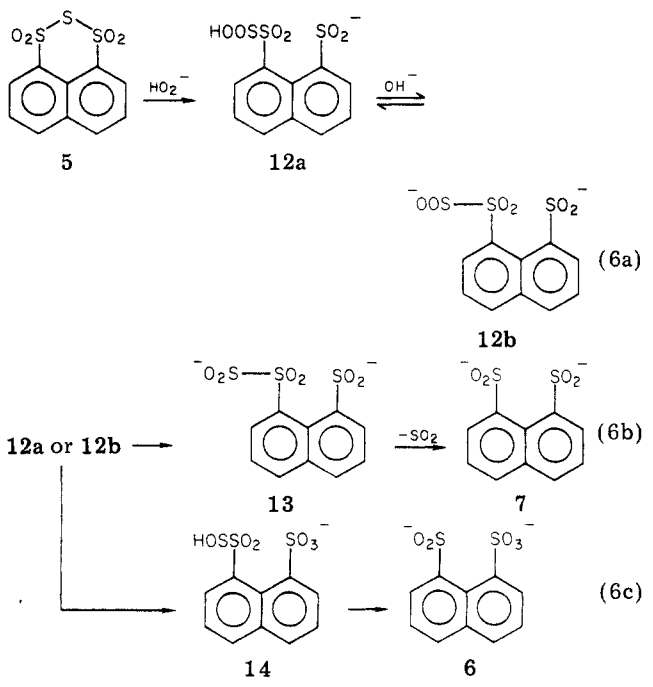
therefore seems reasonable to postulate that the initial step in the reaction of **5** with HO_2^- would be eq 6a. If the persulfenic acid group (SOOH) in **12** isomerizes to a sulfinate (SO_2^-) in the same manner as does **11**, this would give **13** (eq 6b). Loss of sulfur dioxide from **13** would

(3) Chau, M. M.; Kice, J. L. *J. Org. Chem.* **1977**, *42*, 3265.

(4) Besides **8** and **9** a small amount of **1** was also isolated from the chromatography. Since **1** is not water soluble, it cannot have been present in the initial reaction products. Its probable origin is the known[3] reaction of HSO_3^- with sulfinyl sulfone **10**. Previous work[5] has shown that significant amounts of **10** are present in equilibrium with naphthalene-1,8-disulfinic acid even in media of quite high water content.

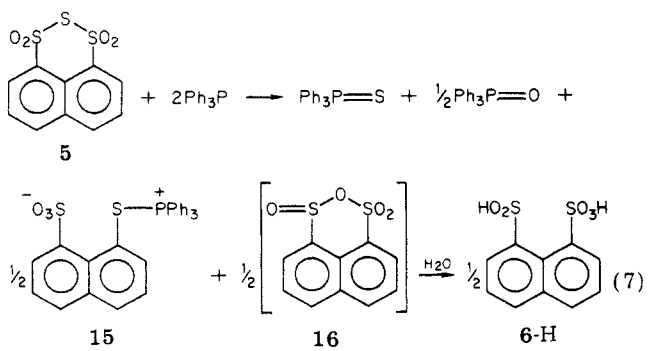
(5) Kice, J. L.; Margolis, H. C. *J. Org. Chem.* **1975**, *40*, 3623.

(6) Kice, J. L.; Rogers, T. E.; Warheit, A. C. *J. Am. Chem. Soc.* **1974**, *96*, 8020.



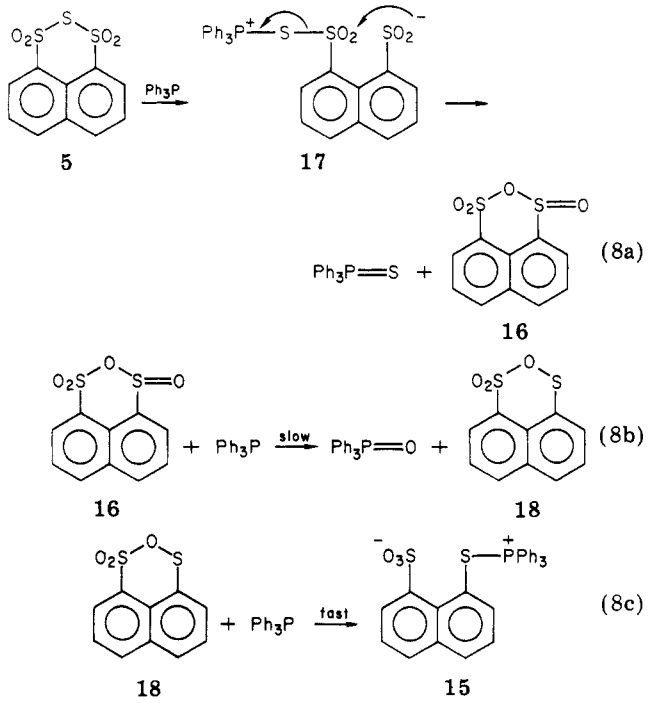
probably be very rapid, giving **7**. Since oxidation of **7** by HO_2^- is not observed in the reaction of **1** with alkaline hydrogen peroxide,[2,5] such a pathway for the formation of **6** in the present system seems unlikely. We therefore tentatively suggest that an intramolecular redox reaction of **12** (eq 6c), which gives **14**, is competitive with its isomerization to **13**. That the SO_2SOH group in **14** would be converted in alkaline solution to an SO_2^- group is expected, given the behavior of a similar functionality in the alkaline hydrolysis of **5** (vide infra).

Reaction of 5 with Triphenylphosphine. Since triphenylphosphine is an excellent thiophile, it might be expected to react readily with **5**, and this indeed proves to be the case. Reaction of **5** (0.015 M) with triphenylphosphine (0.03 M) in toluene at room temperature leads to the formation of a precipitate plus two toluene-soluble products, triphenylphosphine sulfide (0.99 mol/mol of **5**) and triphenylphosphine oxide (0.5 mol/mol of **5**). Partitioning of the precipitate between chloroform and water gives an aqueous layer containing naphthalene-1-sulfinic-8-sulfonic acid (0.47 mol/mol of **5**); this acid was positively identified by conversion to the dimethyl ester (**8**) by using diazomethane. The chloroform layer yields a compound, $C_{28}H_{21}O_3PS_2$ (0.5 mol/mol of **5**), for which the infrared (strong band at 1200 cm^{-1}, SO_3^-) and ^{31}P NMR (44.3 ppm downfield from H_3PO_4, P present as $-P^+<$) spectra suggest the zwitterionic phosphonium salt structure **15**. The stoichiometry of the reaction under these conditions therefore appears to be as shown in eq 7, with the

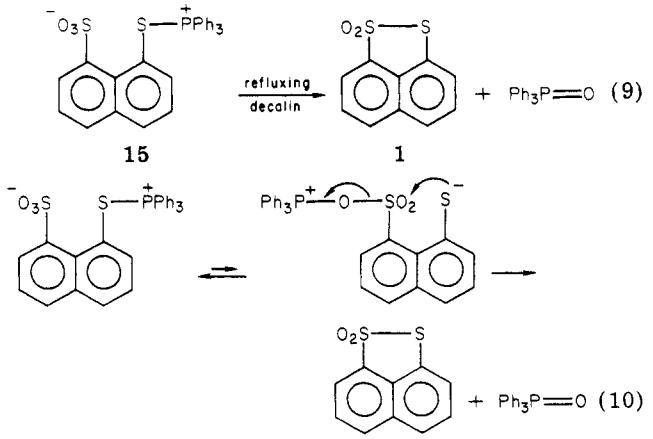


mixed anhydride **16** being converted to naphthalene-1-sulfinic-8-sulfonic acid when the precipitate is treated with water. When the reaction is carried out by using a 3:1 molar ratio of Ph_3P to **5**, the yield of $Ph_3P{=}O$ increases to 1.0 mol/mol of **5**, and the amount of **6**-H (and therefore **16**) decreases to only 0.1 mol/mol of **5**.

These various observations can be satisfactorily explained by a mechanism (eq 8) having the following features: (a) initial attack of Ph_3P on the dicoordinate sulfur of **5** to give **17**, which then collapses to **16** with expulsion of $Ph_3P{=}S$ (eq 8a); (b) deoxygenation of **16** by a second molecule of Ph_3P, giving $Ph_3P{=}O$ and **18** (eq 8b); (c) rapid attack of a third molecule of triphenylphosphine on **18** to give **15** (eq 8c). The increase in the yield of $Ph_3P{=}O$ and the large decrease in the yield of **16** when a 3:1 molar ratio of Ph_3P to **5** is used require that the rate of eq 8c be much faster than that of eq 8b.



At the temperature of refluxing decalin the zwitterionic phosphonium salt **15** undergoes thermolysis cleanly and fairly rapidly (~0.5 h) to **1** (80%) and $Ph_3P{=}O$ (72%; eq 9). The mechanism for this decomposition is not known. One possibility would be a sequence such as that in eq 10.

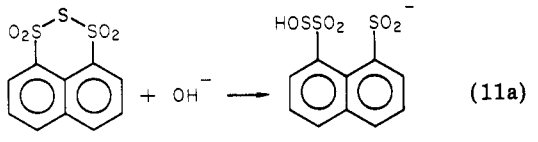


Alkaline Hydrolysis of 5. In alkaline aqueous dioxane **5** undergoes hydrolysis; about 3 equiv of OH^- are consumed per mole of **5** reacting. When the final solution is concentrated and then acidified to pH <1, the following occur: (a) the odor of sulfur dioxide is evident over the solution;

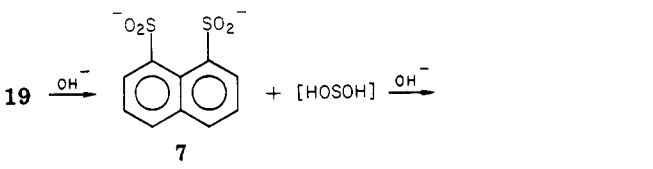
(b) a precipitate forms that consists of a mixture (separable by preparative TLC) of **10** (the "anhydride" of naphthalene-1,8-disulfinic acid) and thiosulfonate **1**. In solution is a small amount of naphthalene-1,8-disulfinic acid. Yields of these various products (mol/mol of **5**) are as follows: **10** (0.55), **1** (0.26), naphthalene-1,8-disulfinic acid (0.02).

The formation of **10** and naphthalene-1,8-disulfinic acid indicates[5] that an equivalent amount of the disulfinate **7** is present in the solution prior to acidification; the presence of SO_2 shows that sulfite is present. Since **10** is known[3] to react readily with sulfite in acid solution to yield **1**, the **1** isolated probably represents additional **10**, formed from **7** upon acidification,[5] that undergoes reaction with sulfite before it has a chance to precipitate.

Nucleophilic attack of hydroxide ion on the dicoordinate sulfur of **5** would be expected to give **19** (eq 11a). Since



5 19 (11a)

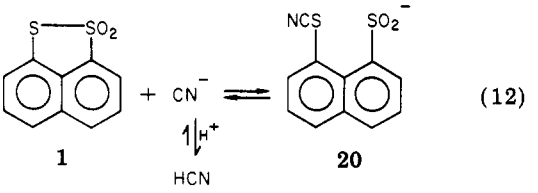


7

SO_3^{2-} + other products (11b)

disulfinate **7** is apparently the virtually exclusive organic product of the reaction, almost all of the **19** produced must go on to form **7**. Exactly how this occurs is not certain, but further reaction with hydroxide ion in the manner shown in eq 11b is one plausible possibility. Sulfoxylic acid, $(HO)_2S$, would also be formed by this reaction. Apparently it gives sulfite as one of its decomposition products.

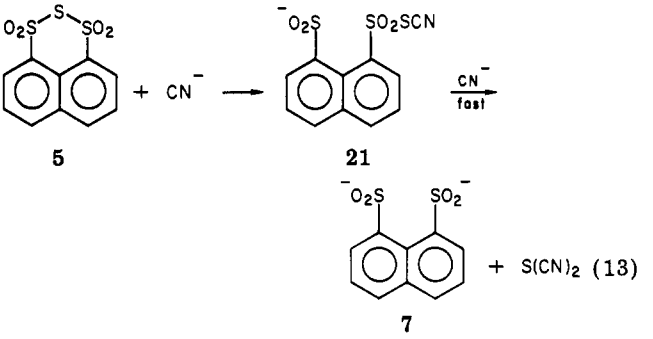
Reaction of 5 with Cyanide Ion. Reaction of cyanide ion with thiosulfonate **1** leads to opening of the thiosulfonate ring and formation of **20** (eq 12).[2] Upon acidification of the reaction solution with a buffer of pH low enough to protonate CN^- completely to HCN, the ring-opening reaction is reversed, and **1** is *quantitatively* regenerated.[2]



1 20 (12)

Addition of CN^- (1×10^{-4} M) to a solution of **5** (1×10^{-4} M) in 60% dioxane (v/v) leads to a rapid decrease in the absorption maximum for **5** at 322 nm to approximately half its original intensity. Addition of a second increment of 1×10^{-4} M CN^- results in further rapid change and the complete disappearance of the peak at 322 nm. Further additions of CN^- beyond that point have no effect. The final spectrum is the same as that of a 1×10^{-4} M solution of **7**. If after the first addition of 1×10^{-4} M CN^- the solution is acidified with a chloroacetate buffer, there is no regeneration of **5**.

Initial reaction of CN^- with **5** should give **21** (eq 13). Since 2 equiv of CN^- are required for complete reaction with **5** and since both equivalents are consumed rapidly, the failure of **5** to be regenerated when the solution is



acidified after addition of the first equivalent of cyanide would seem to be most simply explained by assuming that the reaction of **21** with a second mole of cyanide ion to give **7** is faster than its rate of formation from **5**. This explanation is also consistent with the specific character of the changes in the absorption spectrum of the solution observed upon addition of the first 2 equiv of cyanide.

Experimental Section

Naphtho[1,8-*cd*]-1,2-dithiole 1,1-Dioxide (1). This was prepared in greatly improved yield by modifying somewhat the original procedure of Zweig and Hoffman[7] such that a solution containing a greater ratio of sulfur (8.5 g) to $Na_2S \cdot 9H_2O$ (37 g) was used in the reaction with the diazonium salt (20 g) of 1-amino-8-naphthalenesulfonic acid. This leads to the formation of a trisulfide disulfonic acid rather than the disulfide disulfonic acid obtained by Zweig and Hoffman.[7] Refluxing the disodium salt of the trisulfide disulfonic acid with thionyl chloride gave **1** (mp 150–151 °C) after recrystallization from 2-propanol (lit.[7] mp 148–149 °C) in 49% overall yield.

Naphtho[1,8-*cd*]-1,2,3-trithiin 1,1,3,3-Tetraoxide (5). Naphtho[1,8-*cd*]-1,2-dithiole 1,1,2-trioxide (**10**) was prepared from **1** by the procedure described by Chau and Kice.[3] Sulfinyl sulfone **10** (0.21 g) and 1.75 mL of 1 N sodium hydroxide were mixed together, and after the sulfinyl sulfone had dissolved and reacted, the solution was evaporated to dryness. The residue of disodium naphthalene-1,8-disulfinate (**7**) was washed with ethanol and dried under reduced pressure. It was then suspended in dry chloroform (30 mL), and 55.2 μL of pure sulfur dichloride (SCl_2) was added. The mixture was stirred at room temperature for 5 min. The reaction mixture was then washed with water, and the chloroform layer was separated, dried over $MgSO_4$, and evaporated to dryness. The residue was recrystallized from toluene, giving 0.160 g (64%) of **5**: mp 241–243 °C; IR (KBr) 1500, 1360, 1340, 1215, 1170, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.53 (d, 2 H), 8.30 (d, 2 H), 7.80 (t, 2 H); UV (dioxane) λ_{max} 322 (ε 5800), 308 (7000), 304 (8200). Anal. Calcd for $C_{10}H_6O_4S_3$: C, 41.95; H, 2.11; S, 33.59. Found: C, 41.66; H, 2.07; S, 33.36.

Dimethyl Naphthalene-1,8-disulfinate (9). Sulfinyl sulfone **10** (0.12 g, 0.5 mmol) was mixed with several milliliters of methanol, and diazomethane (in Et_2O), in considerable molar excess over **10**, was then added. After the reaction was complete, removal of the solvent gave a residue which TLC (SiO_2; 1:2 EtOAc–CCl_4) indicated was a mixture of the *dl* and meso isomers of dimethyl naphthalene-1,8-disulfinate (**9**). The major isomer could be easily separated in a pure state by dissolving the residue in benzene and then adding petroleum ether: colorless needles; 0.10 g; mp 111–113 °C; IR (KBr) strong bands at 1110 and 945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.58 (dd, 2 H), 8.20 (dd, 2 H), 7.73 (t, 2 H), 3.48 (s, 6 H). Anal. Calcd for $C_{12}H_{12}O_4S_2$: C, 50.67; H, 4.29. Found: C, 50.82; H, 4.32.

The minor isomer of **9** is most easily distinguished from the major isomer by the fact that the singlet associated with its CH_3O groups occurs at δ 3.60, rather than δ 3.48, in the ^1H NMR. From the ^1H NMR spectrum of the mixture the two isomers are estimated to be present in a ratio of 83:17, respectively. In methanol solution in the presence of a trace of methoxide ion both pure isomers undergo rapid equilibration to give the 83:17 equilibrium

(7) Zweig, A.; Hoffman, A. K. *J. Org. Chem.* **1965**, *30*, 3997.

mixture mentioned above. The major isomer is tentatively considered to be the *dl* isomer on the basis that examination of molecular models suggests that the location of the signal for its CH_3O protons would be upfield from that for the CH_3O protons of the meso isomer.

Dimethyl Naphthalene-1-sulfinate-8-sulfonate (8). Naphtho[1,8-*cd*]-1,2-dithiole 1,1,2,2-tetraoxide (**3**; 0.072 g, 0.28 mmol) was dissolved in dioxane, and 0.6 mL of 1 N sodium hydroxide was added. After 1 h the mixture was evaporated to dryness, and the residue was dissolved in a small amount of water. The solution was passed through a column of Dowex 50W-X8 ion-exchange resin. The acidic eluate was carefully evaporated under reduced pressure, and the residue was treated with an ethereal solution of diazomethane. Workup of the ether after the reaction gave 0.075 g (89%) of **8**: mp 105–105.5 °C; IR (KBr) strong bands at 1340, 1190, 1160, 1135, 1110, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48–8.85 (m, 6 H), 3.90 (s, 3 H), 3.58 (s, 3 H). Anal. Calcd for $C_{12}H_{12}O_5S_2$: C, 47.97; H, 4.06. Found: C, 48.18; H, 4.07.

Reaction of 5 with Alkaline Hydrogen Peroxide. To 0.114 g (0.40 mmol) of **5** in 6 mL of dioxane was added a solution consisting of 0.045 mL of 30% hydrogen peroxide, 0.8 mL of 1 N NaOH, and 1.3 mL of water. After 1 h the solution was evaporated to dryness, and the residue was treated with a small amount of water. The water-insoluble portion of the residue (24 mg) was shown to be unreacted **5**. The water-soluble portion of the residue was passed through a column of Dowex 50W-X8 ion-exchange resin, and the acidic eluate was carefully evaporated under reduced pressure. The residue from the evaporation was treated with a small amount of methanol, and then a solution containing excess diazomethane in ether was added. After the diazomethane had reacted, the ether–methanol solution was evaporated to dryness, and the residue was subjected to preparative TLC (SiO_2, 1:2 EtOAc–CCl_4). There were obtained 8 mg of **1**, 37 mg (0.12 mmol) of **9** (usual 87:13 mixture of *dl* and meso isomers), and 40 mg (0.13 mmol) of **8**.

Reaction of 5 with Triphenylphosphine. A solution of 0.50 g (1.75 mmol) of **5** in 90 mL of toluene was mixed with a solution of 0.92 g (3.5 mmol) of triphenylphosphine in 20 mL of the same solvent and allowed to stand for 1 day at ca. 25 °C. The large amount of precipitate that formed during that time was then filtered off. Evaporation of the toluene filtrate gave a residue that was separated by chromatography into triphenylphosphine sulfide (0.51 g, 1.74 mmol) and triphenylphosphine oxide (0.24 g, 0.88 mmol), each identical with a known sample.

The precipitate was dissolved in chloroform, and the chloroform was washed with water. The water was then evaporated under reduced pressure at room temperature, and the residue was treated with an ethereal solution of diazomethane. Upon removal of the ether there was obtained 0.245 g (0.82 mmol) of the diester **8**.

Evaporation of the chloroform layer gave ~0.5 g of a solid which could be recrystallized from isopropyl alcohol to give 0.49 g of **15**·*i*-PrOH: mp 237–240 °C; IR (KBr) strong bands at 1420, 1200, 1170, 1090, 1020 cm^{-1}; ^{31}P NMR ($CDCl_3$) 44.3 ppm (downfield from H_3PO_4). Anal. Calcd for $C_{28}H_{21}O_3PS_2 \cdot C_3H_7OH$: C, 66.40; H, 5.21; P, 5.52; S, 11.43. Found: C, 65.40; H, 5.16; P, 5.71; S, 11.56.

In another experiment **5** (100 mg, 0.35 mmol) was reacted with 0.275 g (1.02 mmol) of triphenylphosphine in 40 mL of toluene. Upon workup of the reaction mixture after 1 day in the fashion described above there were obtained 0.105 g (0.35 mmol) of triphenylphosphine sulfide, 0.150 g (0.37 mmol) of triphenylphosphine oxide, 0.045 g of unreacted triphenylphosphine, only 0.012 g (0.04 mmol) of **8**, and 0.095 g (0.17 mmol) of **15**.

Thermal Decomposition of 15. A sample of **15**·*i*-PrOH (50 mg, 0.089 mmol) was placed in decalin and refluxed under argon for 0.5 h. The decalin was then removed under reduced pressure, and the residue was subjected to preparative TLC (SiO_2/$CHCl_3$), giving **1** (16 mg, 0.072 mmol) and triphenylphosphine oxide (18 mg, 0.064 mmol).

Alkaline Hydrolysis of 5. A sample of **5** (57 mg, 0.2 mmol) was dissolved in 3 mL of dioxane, and 1.5 mL of 1 N sodium hydroxide in 2.6 mL of water was added with stirring. A transient yellow color appeared. After the reaction was complete, the solution was evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of water and acidified to pH <1 with cold 50% sulfuric acid. A precipitate separated, and a slight odor of sulfur dioxide was detected above the solution. The precipitate was subjected to preparative TLC (SiO_2/Me_2CO–$CHCl_3$), giving 10 mg (0.04 mmol) of **1** and 25 mg (0.11 mmol) of **10**.

In another experiment, 0.22 g (0.77 mmol) of **5** was dissolved in 12 mL of dioxane and 6 mL of 1 N sodium hydroxide added. The residue after removal of the solvent was dissolved in a small amount of water and acidified with HCl. The precipitate which separated was filtered off. The filtrate was then evaporated to dryness, and its residue *plus* the precipitate were then mixed with methanol and treated with a solution of excess diazomethane in ether in the same manner as described for the preparation of **9** from **10**. Preparative TLC of the residue remaining after removal of the solvent gave 44 mg (0.20 mmol) of **1** and 0.125 g (0.44 mmol) of the usual equilibrium mixture of *dl* and meso stereoisomers of **9**.

Unsuccessful Attempted Oxidations of 5. In each of these attempted oxidations 0.1 mmol of **5** (29 mg) was dissolved in 1–2 mL of the solvent indicated and treated with the oxidizing agent in the manner listed; **5** was recovered unchanged in essentially quantitative yield in each case.

m-Chloroperbenzoic acid: $CHCl_3$, 0.3 mmol of peracid, room temperature, 1 week. Peroxytrifluoroacetic acid: 0.5 mL of trifluoroacetic anhydride plus 0.018 mL of 30% hydrogen peroxide, room temperature, 5 days. Ozone: 0.2 mmol of O_3 in CH_2Cl_2, -70 °C for 1 h and then allowed to warm to room temperature. Triphenylphosphite ozonide: CH_2Cl_2 solution of oxidant prepared from triphenylphosphite and ozone at -70 °C, 5 h at -70 °C and then allowed to warm to room temperature. *tert*-Butyl hypochlorite: $CHCl_3$, 0.1 mmol of *t*-BuOCl, 5 days at room temperature. Ruthenium tetraoxide: 0.05 mmol of RuO_4 in CCl_4 added to **5** in $CHCl_3$; a precipitate of ruthenium dioxide forms, apparently due to oxidation of $CHCl_3$, since **5** was recovered unreacted. Potassium permanganate: CH_2Cl_2 containing 18-crown-6, 0.13 mmol of $KMnO_4$; a precipitate of MnO_2 forms, but **5** is recovered unreacted. Bromine–1,4-diazabicyclo[2.2.2]octane: acetic acid, 0.1 mmol of Br_2 complex, 40 °C, until bromine color disappeared. Sodium periodate: $CHCl_3$ plus 18-crown-6, 0.1 mmol of sodium periodate, room temperature, several days. $PhI(OAc)_2$: $CHCl_3$, 0.1 mmol of oxidizing agent, room temperature, 5 days.

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Registry No. **1**, 40277-43-8; **3**, 62609-77-2; **5**, 79272-66-5; **6**, 79272-67-6; **7**, 63059-24-5; **8**, 79299-85-7; **9** (isomer 1), 79272-68-7; **9** (isomer 2), 79272-69-8; **10**, 57821-65-5; **15**, 79272-70-1.