IXb, 27193-11-9; IXc, 27193-12-0; IXd, 27193-13-1; XIa, 27193-14-2; XXI, 482-23-5; XXIIIa, 496-08-2.

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Organic Disulfides and Related Substances. 31. Possible Anchimeric Involvement of an Ortho Carboxylate Moiety in Disproportionation of Unsymmetrical *o*-Carboxyphenyl Disulfides[1]

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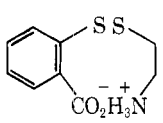
Disproportionation of 2-(phenyldithio)benzoic acid (**2**) to phenyl disulfide and 2,2′-dithiodibenzoic acid is much faster for the salt than for the acid. Among the facts which suggest that the *o*-carboxylate moiety of the salt anchimerically facilitates disproportionation are the following: an increase in rapidity with increasing pH near pH 7; decreased rapidity for the meta isomer; lack of a marked effect of dilution; inhibition of disproportionation by *N*-ethylmaleimide (through trapping of benzenethiolate ion) but acceleration by addition of thiolate ion; accordance with expectation as to the relative rapidity of disproportionation of other dithiobenzoic acids; and, evidence for existence and consistent reactions of *o*-sulfenobenzoic acid anhydride (**5a**) as an unstable intermediate generated by anchimeric displacement of benzenethiolate ion by the *o*-carboxylate moiety.

o-(2-Protoaminoethyldithio)benzoate (**1**) is active as an antiradiation drug.[2] That the methyl ester, the



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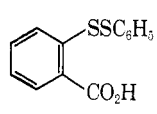


2

meta isomer, and the para isomer of **1** showed no significant antiradiation activity[2a] led us to suspect anchimeric involvement of the carboxylate moiety of **1** with the disulfide linkage. In a similar vein, inactivity of the cyclohexyl analog of **1**[2b] is understandable, since this analog is believed to have trans substituents, which should resist anchimeric involvement. This suspicion of anchimeric involvement was strengthened during work with a phenyl counterpart (**2**) of **1**, since the sodium salt of **2** (**3**) disproportionated far more readily to the two symmetrical disulfides than did **2** itself (eq 1).[3]

$$2 + OH^- \xrightarrow{-H_2O} \underset{\mathbf{3}}{o\text{-}\bar{O}_2CC_6H_4SSC_6H_5} \rightleftharpoons {}^1/_2(o\text{-}\bar{O}_2CC_6H_4S)_2 + {}^1/_2(C_6H_5S)_2 \quad (1)$$

This paper further supports the probability of such an anchimeric involvement in the reaction of eq 1.

The extent of disproportionation of **2** proved to be highly dependent on the pH of the solution (Table I). At pH 14 disproportionation is 95% complete in 0.6 hr (calculated as usual).[4] Attack of the hydroxyl ion on the disulfide bond may be a major path of reaction at high pH.[5] At much lower values of pH, on the other hand, the notable increase in disproportionation with increasing pH points toward increasing anchimeric involvement of carboxylate ion with the disulfide moiety. For example, with a 24-hr reaction period, Table I shows that for the pH sequence 6.4, 6.8, 7.6, and 8.5, the sequence in "disproportionation, %" was 13, 14, 46, and 70.

TABLE I

pH DEPENDENCE OF THE DISPROPORTIONATION OF DISULFIDE **2**[a]

pH[b]	Time, hr	%[c]	pH[b]	Time, hr	%[c]
14	0.6	95	6.8	164	31
8.5	48	81	6.8	73	31
8.5	24	70	6.8	56	26
8.5	3	39	6.8	24	14
8.5	2	32	6.4	216	25
7.6	24	46	6.4	44	17
7.6	24	45[d]	6.4	24	13
7.6	24	39[e]	6.4	18	12
7.6	24	3[f]	6.4	2	3
7.6	24	39[g]	6.4	24	100[h]
			i	*i*	<2

[a] In 10 ml of H_2O (except as noted) at 25–26°; solutions resulted in each instance. [b] Measured both before and after the reaction; not more than 0.4 pH unit change in 216 hr and no change in 72 hr. [c] "Disproportionation, %"; see ref 4. [d] Containing 10 mol % of *N*-ethylmaleimide (**4**). [e] Containing 31 mol % of **4**. [f] Containing 115 mol % of **4**. [g] In 100 ml of H_2O. [h] Containing 10 mol % of $C_6H_5S^-Na^+$ (**6**). [i] After being dissolved completely in 10 ml of AcOH and heated for 119 hr at 100°, **2** was recovered unchanged.[3]

Disproportionation reactions of disulfides can be homolytic, heterolytic, or some combination of these pathways.[6] Although **2** also may be subject to light-induced disproportionation,[3] the carboxylate-assisted re-

(1) (a) Paper XXX: L. Field and P. R. Engelhardt, *J. Org. Chem.*, **35**, 3647 (1970). (b) This investigation was supported by Public Health Service Research Grant AM11685 from the National Institute of Arthritis and Metabolic Diseases. (c) Abstracted from the Ph.D. Dissertation of P. M. G., Jr. (Vanderbilt University, May 1970), which may be consulted for further details. (d) Reported in part at the Southeastern Region Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968, Abstracts, p 98, and at the IVth Symposium on Organic Sulfur, Venice, Italy, June 1970.

(2) (a) R. R. Crenshaw and L. Field, *J. Org. Chem.*, **30**, 175 (1965); (b) L. Field and P. M. Giles, Jr., *J. Med. Chem.*, **13**, 317 (1970).

(3) L. Field and P. M. Giles, Jr., *J. Org. Chem.*, **36**, 309 (1971).

(4) L. Field, T. C. Owen, R. R. Crenshaw, and A. W. Bryan, *J. Amer. Chem. Soc.*, **83**, 4414 (1961).

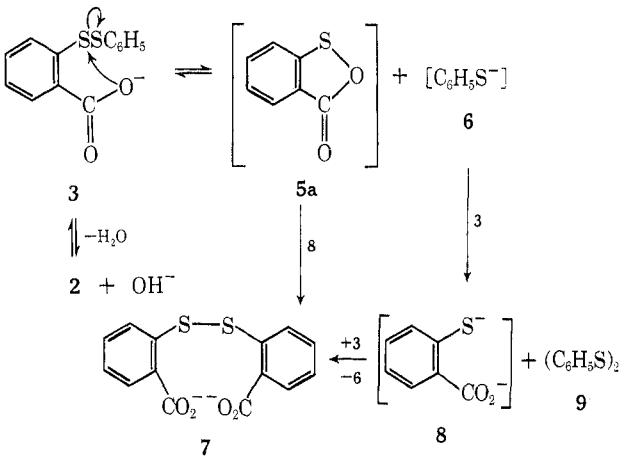
(5) For a discussion of the effect of base on symmetrical disulfides and of the resistance of sodium 2,2′-dithiodibenzoate to attack by OH^- even at high pH, however, see J. P. Danehy and K. N. Parameswaran, *J. Org. Chem.*, **33**, 568 (1968).

(6) L. Field, T. F. Parsons, and D. E. Pearson, *ibid.*, **31**, 3550 (1966).

action seems likely to involve mainly heterolytic cleavage, since all of the studies described in this paper were done in the dark.

Scheme I outlines the best rationalization that has

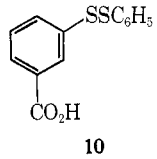
SCHEME I



occurred to us for the disproportionation of **2**, after an accumulation of experiments designed to test possibilities. Scheme I resembles one proposed earlier in which an anchimeric effect of a β-amino moiety was invoked.[7] We regard Scheme I as a formulation of several processes likely to play a role and not as a detailed exposition of mechanism. The reactions involved in the disproportionation of **2** undoubtedly are quite complex in their dependence on ionization and displacement equilibria; for example, the effect of the increase in pH mentioned above may result partly from an increase in the amount of thiolate ion relative to that of thiol. Even so, the experimental facts which have emerged in testing consequences of Scheme I have predictive value *per se*, quite apart from the support they seem to lend to the general credibility of Scheme I. Some experiments suggested during the evolution of Scheme I are outlined in the sections which follow, along with a discussion of their predictive value and their apparent consistency with Scheme I.

(1) A pH dependence like that seen in Table I would be expected in Scheme I.

(2) The meta isomer of **2** should be less susceptible to disproportionation, at least to the extent that its disproportionation fails to be initiated *via* an anchimeric effect. At pH 6.8, the salt of **10** is 10% disproportionated in 24 hr (14% for **2**) and 18% after 73 hr (31% for **2**). That differences are not greater may result from



10

the known considerably greater susceptibility of *m*-carboxyphenyl disulfides to attack by hydroxyl ion,[5] which of course would lead to thiolate ion.

(3) Since the conversion of **3** to **5a** is intramolecular, the extent of disproportionation should not be much affected by concentration if this step is slow relative to the thiolate interchange. When the disproportionation of **2** at pH 7.6 was carried out at one-tenth the usual concentration, the extent of disproportionation decreased only from 46 to 39% (see Table I).

(4) Trapping of the thiolate ion **6** should greatly inhibit disproportionation, since **6** has a chain-propagating function in Scheme I. A similar function for the dianion **8** seems likely, although it should be less important because of the lower acidity of **8** (pk_{SH} 8.20 contrasted with pK_{SH} 6.62 for **6**);[5] facile protonation of the thiolate ion of **8** thus should reduce its relative availability.

When 10 mol % of *N*-ethylmaleimide (**4**) was added at pH 7.6 (Table I), the disproportionation of **2** (46%) was not affected (45%), but 31 mol % of **4** began to cause an effect (39%) and 115 mol % virtually shut down the disproportionation (3%). Thiolate ion thus certainly seems to be implicated in the disproportionation of **2**.

As an incidental matter, this effect with the imide **4** led us to try it with disproportionations studied earlier of aminoalkyl aryl disulfide hydrochlorides[6] and of 2-(*n*-decylamino)ethyl benzyl disulfide hydrochlorides.[7] The first of these evidently involves either a lack of marked dependence on thiolate–disulfide interaction or ineffective trapping, since the results were quite different from those with **2**. For example, we observed for 2-(phenyldithio)ethylamine hydrochloride (**11**), 80% disproportionation without **4** and 71% with 100 mol %

$C_6H_5SS(CH_2)_2NH_3^+Cl^-$

11

p-$CH_3C_6H_4CH_2SS(CH_2)_2NH_2^+$-$n$-$C_{10}H_{21}Cl^-$

12

of **4** (160 hr, 68°). With *p*-methylbenzyl 2-(*n*-decylamino)ethyl disulfide hydrochloride (**12**), results were more as expected, 35% without **4** and only 1% with 100 mol % of **4** (100°, 480 hr).

The results in Table I for the early phases of reactions seem consistent with first-order reactions, as did those with **11** and **12** (for which the significance still is uncertain),[6,7] but the different effects of **4** imply that the disproportionation of **2** may differ from that of **11**, although perhaps not from that of **12**.

(5) Addition of the thiolate ion **6** should accelerate disproportionation. Table I shows that disproportionation increased from 13 to 100% when 10 mol % of **6** was added (pH 6.4, 24 hr).

(6) The *p*-chlorophenyl analog of **2** (**13**) might be expected to disproportionate more rapidly than **2**, if the generation of thiolate ion **6** were rate determining, since Parker and Kharasch report that "the greater the anionic stability of the displaced mercaptide ion, the more susceptible to scission is the parent disulfide,"[8] and since *p*-chlorothiophenol has a pK_{SH} of 5.9 in water, compared with 6.62 for thiophenol.[9] Conversely, 2-(*n*-butyldithio)benzoic acid (**14**) should react less rapidly than **2** (1-butanethiol has a pK_{SH} of 11.51).[9]

n-Butyl disulfide was isolated in 40% yield using the sodium salt of **14** (24 hr, 25°, pH 8.5; Table I shows that **3** underwent 70% disproportionation under these conditions). The sodium salt of the *p*-chlorophenyl analog

(7) M. Bellas, D. L. Tuleen, and L. Field, *J. Org. Chem.*, **32**, 2591 (1967).

(8) A. J. Parker and N. Kharasch, *J. Amer. Chem. Soc.*, **82**, 3071 (1960).

(9) J. P. Danehy and K. N. Parameswaran, *J. Chem. Eng. Data*, **13**, 386 (1968).

13 was 90% disproportionated under the same conditions.

At first, the stability of the aminoalkyl disulfide **1** seemed to contradict the views above. The remainder of this section deals with experiments carried out in an effort to clarify this point. 2-Aminoethanethiol has the rather low pK_{SH} of 8.23;[9] **1** might therefore be thought to undergo disproportionation not a great deal less rapidly than **2**. However, disulfide **1** was only 1% disproportionated under conditions which resulted in 46% disproportionation of **2** (pH 7.6, 24 hr, 25°). Furthermore, **1** is less reactive than its hydrochloride,[2a] not more so. We are inclined to attribute these paradoxes to anomalies with **1**. In part, a tight ion-pair involvement of the carboxylate ion of **1** with an ammonium moiety may hinder its usual anchimeric function. In part also, since **2** undergoes an essentially irreversible reaction driven by sparing solubility of phenyl disulfide (**9**) in water (*vide infra*), the reversible reaction of **1** may be slowed relative to that of **2** by accumulation of **15** (eq 2), which is soluble.

$$\underset{\mathbf{15}}{(o\text{-}\bar{O}_2CC_6H_4S)_2(H_3\overset{+}{N}CH_2CH_2S)_2} \rightleftharpoons 2\,\underset{\mathbf{1}}{o\text{-}\bar{O}_2CC_6H_4SSCH_2CH_2NH_3^+} \quad (2)$$

With respect to this matter of reversibility, it is true that the disproportionation of **2** does not readily go to completion at pH 6.4–8.5 (although it does do so at higher pH). This result *could* indicate attainment of equilibrium, but it seems more likely to be caused by an accumulation of a species such as **7** in such concentration as to compete with **3** for thiolate ions (**6**). In this respect therefore, **2** resembles **1** except that only one soluble symmetrical disulfide is accumulating rather than two, as a competitor for thiolate ions. To test these points, examination of the extent of reversibility within Scheme I and eq 2 was desirable. The equilibrium with **2** (Scheme I) was examined by approaching the reaction of Scheme I from the product side. When typical amounts of **7** and **9** were maintained in water at 25° for 24 hr at pH 7, *i.e.*, under conditions for 14–46% disproportionation of **2**, only **7** and **9** could be isolated, although tlc (after acidification) did suggest the presence of a trace of **2**. Thus, although the possibility of an equilibrium cannot be ignored, the precipitation of **9** surely tends to force **3** toward **7** and **9**.

The slower disproportionation of **1** than of its hydrochloride was tentatively attributed earlier to the solubility of the disproportionation product formed by **1** (*i.e.*, cystamine 2,2′-dithiodibenzoate, **15**);[2a] the hydrochloride leads to only one soluble product, cystamine dihydrochloride, since the other (2,2′-dithiodibenzoic acid) precipitates. To confirm the supposed reversibility of eq 2, the salt **15** was heated in water until reaction was complete. The sparingly soluble **1** then could be separated in 41% yield, permitting the estimate that K for eq 2 approximates 2 (the statistical value is 4).[10]

(7) *o*-Sulfenobenzoic acid anhydride (**5a**), in common with sulfenyl species in general, should be highly reactive and unstable, although it might persist long enough for its existence to be corroborated; **5a** has been proposed as an intermediate in the oxidation of 2,2′-dithiodibenzoate ion.[11] A few sulfenyl carboxylates having the moiety –SOC(O)– are known.[12] Most are quite unstable and exhibit ir absorption at 1710–1780 cm^{-1}.[12b]

The preparation of a red oil (**5b**) that appeared to be largely **5a** was achieved as shown by eq 3. During 0.5

$$o\text{-}HO_2CC_6H_4SH + Cl_2 \longrightarrow [o\text{-}HO_2CC_6H_4SCl] \xrightarrow{Et_3N} \mathbf{5b} + Et_3NH^+Cl^- \quad (3)$$

hr after preparation, this oil (**5b**) oxidized iodide to iodine (86% of expectation), showed strong ir absorption appropriate for **5a** at 1790 cm^{-1}, and had a mass spectrum peak at m/e 152 of relative abundance 25% (calcd for **5a**, 152). The oil contained no chlorine, thus eliminating a sulfenyl chloride as a cause of its reactions. Sulfenyl character nevertheless could be demonstrated by conversion of **5b** by thiophenol to **2** (81%), and by the dianion **8** (after acidification) to the conjugate acid of **7** (29%); these reactions also support the feasibility of the two similar processes in Scheme I. After 0.5 hr **5b** began to stiffen, and both the ir band at 1790 cm^{-1} and the peak at m/e 152 began to shrink. After 24 hr, **5b** had solidified. Repeated recrystallization then gave red solid (**16**) with a constant melting point of 110–114°. The **16** (in solution) no longer oxidized iodide to iodine; it had ir absorption at 1680 cm^{-1} but not at 1790 cm^{-1}, a mass spectrum peak of relative abundance only 1% at m/e 152, and an elemental analysis roughly consistent with a polymer of **5a**; unfortunately, sparing solubility of **16** precluded determination of its molecular weight.

Experimental Section[13]

Materials.—Disulfides **1**,[2a] **2**,[3] **14**,[3] and **15**,[2a] and *o*-carboxyphenyl *o*-carboxybenzenethiolsulfonate[3] were prepared according to established procedures. Disulfide **11** was kindly provided by Dr. T. F. Parsons[6] and disulfide **12** by Dr. M. Bellas.[7] *o*-Mercaptobenzoic acid was recrystallized from EtOH–H_2O,[14] mp 165–166° (lit.[14] mp 163–164°). All other materials were used as purchased. The pK_a of disulfide **2** determined by titration using a Model 72 Beckman pH meter was 6.5 in 3:7 EtOH–H_2O and 8.0 in 1:1 EtOH–H_2O. The mass spectrum of **2** was as follows: m/e (rel intensity) 264 (6), 263 (8), 262 (46), 155 (6), 154 (12), 153 (100), 152 (37), 136 (10), 111 (3), 110 (8), 109 (65), 108 (46), 107 (21), 98 (19), 82 (10), 77 (12), 69 (31), 65 (35), 63 (12), 51 (17), 50 (12), 45 (17).

Preparation of 3-(Phenyldithio)benzoic Acid (10).—A solution of *m*-mercaptobenzoic acid[2a] (0.77 g, 5 mmol) and phenyl benzenethiolsulfonate[15] (1.25 g, 5 mmol) in EtOH (25 ml) was heated (reflux, 4 hr). Water (100 ml) was added, the solution was extracted with three 50-ml portions of Et_2O, and the combined ethereal extracts were dried ($MgSO_4$). Solvent was removed to give crude **10**, 1.30 g (99%), mp 160–170°. Repeated recrystallization of **10** from MeOH–H_2O and from Et_2O–hexane gave **10**

(10) L. Haraldson, C. J. Olander, S. Sunner, and E. Varde, *Acta Chem. Scand.*, **14**, 1509 (1960).

(11) J. P. Danehy and M. Y. Oester, *J. Org. Chem.*, **32**, 1491 (1967).

(12) (a) A. J. Havlik and N. Kharasch, *J. Amer. Chem. Soc.*, **78**, 1207 (1956); (b) R. E. Putnam and W. H. Sharkey, *ibid.*, **79**, 6526 (1957); (c) J. H. Uhlenbroek and M. J. Koopmans, *Recl. Trav. Chim. Pays-Bas*, **76**, 666 (1957).

(13) Melting points are corrected. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Mass spectra were obtained with an LKB Model 9000 instrument, operating at 70 eV using the direct-inlet system, which was obtained through Science Development Program Grant GU-2057 from the National Science Foundation; we are indebted to Mr. C. Wetter for these spectra. Ir spectra were obtained using a Beckman Model IR-10 with films of liquids and KBr pellets of solids. Solvents were evaporated under reduced pressure with a rotary evaporator. Eastman Chromagram sheet type 6060 (silica gel) was used for tlc (developed at 25° with 9:1 $CHCl_3$–EtOH and then exposed to I_2 vapor in a sealed container).

(14) C. F. H. Allen and D. D. MacKay, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 580.

(15) L. Field and T. F. Parsons, *J. Org. Chem.*, **30**, 657 (1965).

having mp 170–175°: tlc showed only one spot (R_f 0.13); ir (KBr) 3300–2300, 1690, 1590, 1565, 1440, 1300, 900, 740, 720, and 550 cm^{-1}; mass spectrum *m/e* (rel intensity) 264 (10), 263 (17), 262 (100), 198 (6), 155 (6), 154 (9), 111 (3), 110 (12), 109 (64), 77 (8), 69 (17), 65 (30), 51 (9), 45 (8) (*note the absence of m/e 152 which is found in the mass spectrum of* **2**).

Anal. Calcd for $C_{13}H_{10}O_2S_2$: C, 59.51; H, 3.84; S, 24.45. Found: C, 59.71; H, 3.91; S, 24.66.

Preparation of 2-(4-Chlorophenyldithio)benzoic Acid (13).—A solution of *p*-chlorothiophenol (1.45 g, 10 mmol) and *o*-carboxyphenyl *o*-carboxybenzenethiolsulfonate (3.38 g, 10 mmol)[8] was stirred for 1 hr at 25° in 95% EtOH (50 ml). A white solid began to separate after 0.25 hr. Cooling (*ca.* 0°) and filtration gave 2.60 g (88%) of **13** having mp 195–197°. Recrystallization from EtOH–H_2O gave **13** having a constant melting point of 204–206°: tlc gave only one spot (R_f 0.05); ir (KBr) 3200–2300, 1670, 1590, 1560, 1465, 1420, 1315, 1270, 1260, 815, 740, 690, and 640 cm^{-1}.

Anal. Calcd for $C_{13}H_9ClO_2S_2$: C, 52.61; H, 3.06; Cl, 11.95; S, 21.61. Found: C, 52.89; H, 3.11; Cl, 12.01; S, 21.33.

Studies of Disproportionation.—Carefully weighed samples of disulfide **2** (*ca.* 1 mmol) were dissolved in 10 ml of H_2O containing an exactly equivalent amount of NaOH (*ca.* 1 mmol) in 10-ml flasks. The pH of the solution was measured using pHydrion paper (accuracy of ±0.1 pH unit) and was adjusted to the value given in Table I. The flasks were wrapped with aluminum foil for protection from light. They were kept at 25–26° for the time intervals designated in Table I, after which they were chilled in ice and the pH was measured again. "Disproportionation, %" was determined by isolating phenyl disulfide (**9**) formed using filtration (identity and purity were established by melting point, ir, and tlc after recrystallization from hexane) and then by calculation as usual;[4] the results are given in Table I. The disproportionation of the meta isomer **10** was measured similarly, as was that of 2-(*n*-butyldithio)benzoic acid (**14**; *n*-butyl disulfide was isolated by extraction with Et_2O and was identified by ir and tlc) and of 2-(4-chlorophenyldithio)benzoic acid (**13**; *p*-chlorophenyl disulfide was isolated by filtration, recrystallized from hexane, and identified by melting point, ir, and tlc). Disulfide **1** (*ca.* 1 mmol) was dissolved in 10 ml of H_2O (100°) in a 10-ml foil-wrapped flask, and the solution was cooled quickly to 25°; a relatively small amount of the solid **1** precipitated. After 24 hr at 25°, chilling (0°) and filtration gave unchanged **1** in *ca.* 99% yield (identified by melting point and ir). Disproportionation of **11** and **12** were determined essentially as reported earlier,[6,7] with or without dissolved **4**; the symmetrical disulfides were characterized by ir and melting point; "disproportionation, %" was calculated as usual.[4]

Equilibration Studies.—Cystamine 2,2′-dithiodibenzoate (**15**) (0.41 g, 0.90 mmol) in H_2O (10 ml) was heated at 100° for 72 hr. The solution was cooled (0°), and crude **1** (very sparingly soluble) was separated by filtration. Recrystallization from H_2O (100°) gave 0.17 g (41%) of material identical with authentic **1** by ir, mp 202–204° dec (lit.[2a] mp 205° dec and 198–200° dec). After 144 hr, an identical sample of **15** again yielded 0.17 g (0.74 mmol) of **1** thus confirming that equilibrium had been achieved in 72 hr; hence K for eq 2[10] = $[\mathbf{1}]^2/[\mathbf{15}][\mathbf{15}] = [0.74]^2/[0.90 - 0.5\cdot(0.74)]^2 = ca.\ 2$.

In the study of the reversibility within Scheme I, phenyl disulfide (**9**, 1.09 g, 5.0 mmol) was suspended in a solution of salt **7** (1.75 g, 5.0 mmol) in H_2O (100 ml). After 24 hr (pH 7, 25°), disulfide **9** was isolated by filtration (1.03 g, 95% recovery, identified by melting point and ir). The filtrate was acidified (pH 1, 10% HCl) and extracted (Et_2O). Tlc showed two spots, R_f 0.00 and 0.19, the former corresponding to the conjugate acid of **7** and the latter to a trace of disulfide **2** (**2** being done concurrently).

Possible Existence of 5a. A. Preparation of 5b.—*o*-Mercaptobenzoic acid (5.00 g, 32.4 mmol) was suspended in CH_2Cl_2 (70 ml) and cooled to 0°. Chlorine (1.61 ml, 2.62 g, 35 mmol) was added slowly (0.5 hr) with stirring. Dry N_2 then was swept through the solution until no HCl or Cl_2 was evident. Triethylamine (4.55 ml, 3.28 g, 32.4 mmol) in CH_2Cl_2 (50 ml) was added (0.25 hr). After 3 hr at 0° the solution was washed twice with 100-ml portions of cold H_2O [triethylammonium chloride was recovered from the H_2O wash (3.34 g, 75% yield), identical with authentic material by melting point (253–255°) and ir], and the organic layer was dried ($CaSO_4$). Evaporation of the solvent below 25° gave a red oil (**5b**), presumed to be largely **5a**: 4.59 g (93%); ir 1790 cm^{-1} (C=O); negative Beilstein test. A sample of **5b** (0.1900 g, 1.25 mequiv if pure **5a**) liberated 1.08 mequiv of I_2 (86%) when treated with excess KI in a modification of the procedure of Kharasch and Wald;[16] this technique has been used for the assay of sulfenyl carboxylates.[12a,16] The mass spectrum of **5b** (peaks above *m/e* 152 were small) was as follows: *m/e* (rel intensity, assignment) 154 (1), 153 (3), 152 (25, $C_7H_4O_2S$), 104 (100, C_7H_4O), 96 (20), 95 (6), 77 (11), 76 (76, C_6H_4), 75 (16), 74 (20), 73 (9), 70 (21), 69 (30), 63 (6), 62 (5), 61 (5), 58 (5), 50 (60), 49 (9), 48 (16); ir (NaCl plates) 3500–2300, 1790, 1700, 1590, 1440, 1270, 1220, 1150, 1020, 990, 890, and 750 cm^{-1}.

The solidified oil which resulted after **5b** had stood at *ca.* 25° for *ca.* 24 hr was recrystallized repeatedly (Et_2O–hexane and MeOH–H_2O) to give material **16** having a constant melting point of 110–114°. A sample of **16** did not liberate I_2 from KI; the ir and mass spectra are mentioned in the discussion.

Anal. Calcd for polymer of $C_7H_4O_2S$: C, 55.25; H, 2.65; S, 21.08. Found: C, 54.56; H, 3.82; S, 20.16.

B. Reaction of 5b with Thiols.—The red oily **5b** (4.03 g, 26.6 mmol if pure **5a**) was stirred with thiophenol (2.69 ml, 26.2 mmol) in EtOH (50 ml). Water (100 ml) was added after 1 hr; solid **2** which precipitated amounted to 5.63 g (81%, based on thiophenol), mp 190–195° dec. Recrystallization from Et_2O–pentane and from EtOH–H_2O gave **2** with a constant melting point of 198–199° dec (*identical with authentic* **2** *by ir and tlc*) (lit.[3] mp 197–198.5° dec).

Another sample of **5b** (1.92 g, 12.6 mmol if pure **5a**) was added in one portion with stirring to H_2O (50 ml) containing the dianion **8** [2.52 g, 12.6 mmol, prepared by neutralizing *o*-mercaptobenzoic acid (12.6 mmol, in MeOH) with NaOMe (25.2 mmol, in MeOH) and carefully removing the solvent]. After the mixture had been stirred at 25° for 0.25 hr, acidification (pH 1, 10% HCl) gave a mixture of *o*-mercaptobenzoic acid and 2,2′-dithiodibenzoic acid, which was separated by fractional recrystallization from EtOH–H_2O. The 2,2′-dithiodibenzoic acid produced (1.10 g, 29%) had mp and mmp 285–290° dec (identical with authentic material by ir) (lit.[17] mp 287–288°). A sample of *o*-mercaptobenzoic acid alone did not react under comparable conditions in a control experiment (tlc and melting point unchanged).

Registry No.—**2**, 26929-62-4; **5**, 27396-44-7; **10**, 27396-45-8; **13**, 27396-46-9.

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