visible. Dilution with acetone (170 ml), in which acrylamide but not polyacrylamide is soluble,[29] gave a small amount of fluff, but cooling and filtration resulted only in 0.125 g (maximum polymerization, *ca.* 1%).

B.—Acrylamide (9.0 g) and the disulfide **4** (0.222 g) in 20 ml of water were irradiated as usual for 1 hr. The solution became viscous and rubbery solid formed on the flask wall. Liquid was decanted, and the mass of solid was dried under vacuum (18 hr) to yield a hard solid weighing 8.82 g (98% polymerization).

Repetition of the experiment without **4** resulted in no signs of polymerization. Dilution with 170 ml of acetone resulted in opalescence, and chilling gave only 0.6 g of fluff (maximum polymerization, *ca.* 7%).

C.—A 0.5 *M* solution of disulfide **4** (0.222 g in 2 ml of water) in a 0.1-cm cell was irradiated at room temperature from a distance of 5 cm with the usual source. No epr signal developed at 9.5 kMc using a V 4548 aqueous solution sample cell in a V 4531 multipurpose cavity. The instrument was equivalent to a Varian 4502-00 audiomodulated epr spectrometer. The range was 2.9–3.5 kgauss.[30]

Acknowledgment.—We wish to record our thanks for helpful and stimulating discussion to Professors C. K. Ingold and D. L. Tuleen and to Doctors J. R. Van Wazer and Harold Weingarten.

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[29] J. R. Cox, Jr., C. L. Gladys, L. Field, and D. E. Pearson, *J. Org. Chem.*, **25**, 1083 (1960).

[30] We are indebted for this measurement to Professor Walter Bouldin and Mr. Robert Hankla of the Department of Physics at Vanderbilt University.

Organic Disulfides and Related Substances. XIX. Alkyl and Aryl Dithiosulfites[1a,b]

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Typical symmetrical and unsymmetrical dithiosulfite esters, RSS(O)SR′, were prepared. Two moles of *t*-butyl dithiosulfite decompose cleanly when heated to give 1 mole each of *t*-butyl disulfide, *t*-butyl trisulfide, and sulfur dioxide; this decomposition seems general for dithiosulfites. Most of the dithiosulfites studied proved to be quite unstable, the relative stability usually decreasing in the order *t*-alkyl ≫ aryl > *sec*-alkyl ≫ primary alkyl (usually not isolable). Decomposition follows first-order kinetics, is strongly catalyzed by sulfur dioxide, and involves scrambling of groups. In their reactions with a thiol, an enolate, and alkali, dithiosulfites resemble thiolsulfonate and thiolsulfinate esters, RSO_2SR and RS(O)SR.

Several authors have reported dithiosulfites, $(RS)_2SO$, but with little or no characterization.[2] Dithiosulfites also have been postulated as intermediates in the decomposition of amidothiosulfites, RNHS(O)SR.[3] Only recently, however, have two reasonably stable dithiosulfites been isolated and characterized, *t*-butyl dithiosulfite (**1**)[4a,b] and dicyano-1,2,3-trithiole-2-oxide(**2**).[4c-e]

Our early efforts to synthesize dithiosulfites were hampered by facile decomposition which seemed characteristic of the class. As a prelude to further synthetic work, therefore, the nature of the decomposition was examined with *t*-butyl dithiosulfite (**1**) as a model. If the decomposition were understood, there was good prospect of assessing relative stabilities of dithiosulfites and consequently of choosing those most likely to be stable enough to warrant preparative effort.

In preparing the model (**1**), which ultimately was obtained in a purer state than heretofore,[4a] modification of the method of Wolff proved the most satisfactory of a number of approaches tried.[4] This modification involved addition of the thiol and pyridine to an equivalent quantity of thionyl chloride, as shown by eq 1.

$$2RSH + SOCl_2 \xrightarrow{C_5H_5N} RSS(O)SR \tag{1}$$

Ether was used as a solvent because of its adaptability with structures of interest, but hydrocarbons may be better when they can be used.[4] The inverse procedure, in which thionyl chloride is added to the thiol and pyridine, probably would favor formation of disulfide by thioalkylation (*vide infra*). Use of the sodium salt of the thiol with thionyl chloride (in the absence of pyridine) afforded no dithiosulfite.

Although the ester **1** is quite stable at 100°, at 185° total decomposition ensued in less than 1 hr. Analysis of the products revealed that the reaction is that of eq 2.

$$2(RS)_2SO \longrightarrow RSSR + RSSSR + SO_2 \tag{2}$$

The weight of the mixture of sulfides was 96% of that required by eq 2, and the ratio of *t*-butyl disulfide to trisulfide was 1 ± 0.1 by gas–liquid partition chromatographic (glpc) analysis. Sulfur dioxide amounted to 96% of 1 mole for each 2 of dithiosulfite. Heating of **1** at 200° in a glpc column showed that total peak area comprised 5% **1**, 42% disulfide, and 48% trisulfide; at other temperatures, the essentially 1:1 ratio of di- to trisulfide persisted. Studies of the thermal decomposition of isopropyl, *n*-butyl, and phenyl dithiosulfite suggest the generality of eq 2.

The products of eq 2 suggested a method for comparing the stabilities of dithiosulfites without extensive purification. Syntheses were accomplished as usual, and the crude reaction mixtures were washed free of as many contaminants as possible. Ether was removed and the residues then were heated at 100°. The time required for the characteristic strong infrared absorption of the SO moiety (at 1110–1145 cm^{-1}) to diminish to one-half of its original value was determined. This half-life, although approximate, furnished an index of

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[1] (a) This investigation was supported by the U. S. Army Medical Research and Development Command, Department of the Army, under Research Contract DA-49-193-MD-2030. Abstracted from part of the Ph.D. dissertation of W. B. L., Vanderbilt University, Aug 1965; (b) Paper XVIII: L. Field, T. F. Parsons, and D. E. Pearson, *J. Org. Chem.*, **31**, 3550 (1966); (c) National Defense Education Act Fellow, 1961–1964.

[2] (a) M. M. Richter, *Ber.*, **49**, 1026 (1916); (b) P. C. Guha and M. N. Chakladar, *Quart. J. Indian Chem. Soc.*, **2**, 318 (1925); (c) Y. Mollier and N. Lozac'h, *Bull. Soc. Chim. France*, **19**, 1076 (1952).

[3] G. Kresze and H. P. Patzschke, *Ber.*, **93**, 380 (1960).

[4] (a) W. F. Wolff, U. S. Patent 3,015,670 (1962); *Chem. Abstr.*, **56**, 15,366 (1962); (b) W. F. Wolff, U. S. Patent 3,017,505 (1963); *Chem. Abstr.*, **58**, 11221 (1963); (c) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4772 (1962); (d) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. C. Roland, and T. L. Cairns, *ibid.*, **84**, 4746 (1962). (e) NOTE ADDED IN PROOF.—P. W. Schenk, R. Steudel, and J. Bilal have recently reported preparation and decomposition of 2-naphthyl dithiosulfite: *Angew. Chem. Intern. Ed. Engl.*, **5**, 673 (1966).

stability ($t_{1/2}$). Since the decomposition was nearly quantitative, the amount of sulfur dioxide evolved should be a measure by eq 2 of the amount of dithiosulfite actually present; the amount of sulfur dioxide actually evolved, in relation to that theoretically possible had the synthesis and decomposition proceeded perfectly, is considered to be the per cent yield in formation of the original dithiosulfite (yield of SO_2). Table I summarizes the results.

TABLE I

ESTIMATED STABILITIES OF SYMMETRICAL DITHIOSULFITES, $(RS)_2SO$ (100°)

R	$t_{1/2}$, hr	Yield of SO_2, %	λ_{SO}, cm^{-1}
t-Butyl	>22	...	1110
t-Amyl	~48	...	1110
2-Naphthyl	4	63	1135
Phenyl	2.5	53	1125
p-Chlorophenyl	2.5	75	1135
p-Tolyl	2	75	1130
o-Chlorophenyl	1	31	1140
p-Methoxyphenyl	0.75	38	1125
Neopentyl	0.75	38	1110
o-Tolyl	0.5	65	1130
o-Methoxyphenyl[a]	0.5	80	1125
o-Nitrophenyl[a]	0.5[b]	45	1115
2,6-Dimethoxyphenyl[a]	0.5[b]	72	1110
4-Methyl-*o*-phenylene[a]	0.5[b]	45	1145
Triphenylmethyl[a]	0.25	4	1120
Isopropyl	0.25	65	1120
Cyclohexyl	0.25	91	1110
$C_6H_5CH{=}C(CO_2CH_3)$[a]	0.25	67	1120
$(CH_3)_2NC({=}S)$[c]	0.25	22	1135

[a] The dithiosulfite partly precipitated when the reaction mixture was washed, and methylene chloride was added to maintain solubility. [b] The dithiosulfite was sparingly soluble in carbon tetrachloride, so a Nujol mull or liquid film was used for infrared spectra. Uniform sample size was doubtful, but since the SO peak was strong at $t = 0$, visible at $t = 0.5$ hr, and absent at $t = 1$ hr, $t_{1/2}$ was assumed to be 0.5 hr, but probably is slightly lower. [c] The potassium salt of dimethyl dithiocarbamate was used in lieu of pyridine; the product was collected by filtration.

In several instances, after removal of solvent, *no* typical infrared absorption and *no* evolution of sulfur dioxide were observed. Dithiosulfites therefore either never formed at all or decomposed before they could be detected. Although these dithiosulfites could not be formed according to eq 1, some of them might be stable if they were once prepared. In these instances, R of $(RS)_2SO$ was *p*-nitrophenyl, 2,3,5,6-tetrafluorophenyl, *o*-aminophenyl hydrochloride, 2-acetamidoethyl, and *n*-butyl. Unpromising results were obtained also with N-acetylpenicillamine methyl ester and 2-methyl-3-acetamido-2-propanethiol, despite the fact that both are tertiary thiols, suggesting culpability of the N-acetyl moiety in these thiols.

The most notable feature of Table I is the remarkable stability of the dithiosulfites derived from *t*-alkyl mercaptans. In general, aryl dithiosulfites seem more stable than *sec*-alkyl, whereas primary alkyl dithiosulfites (except neopentyl) seem not to exist long enough for detection. Electron-withdrawing substituents in the aryl group appear to stabilize the dithiosulfite system, notwithstanding the failures mentioned in synthesis of certain aryl dithiosulfites containing strongly electron-withdrawing substituents (*vide infra*); thus, in Table I, one may compare *p*-chloro *vs.* *p*-methyl *vs.* *p*-methoxy, and *o*-chloro *vs.* *o*-methyl *vs.* *o*-methoxy.

A similar study was made of unsymmetrical dithiosulfites, RSS(O)SR′, in which R was *t*-butyl and R′ was derived from another thiol. This study was made possible by finding that the acid chloride $(CH_3)_3CSS(O)Cl$ was a discrete intermediate in the synthesis of **1**, and that it could be produced in high yield for use *in situ*. The unsymmetrical dithiosulfites were prepared by first forming the intermediate acid chloride and then adding the second thiol together with an acid acceptor. The order of addition was critical. The stability of members of this series was assessed as for the symmetrical series. Table II shows the results.

TABLE II

ESTIMATED STABILITIES OF UNSYMMETRICAL DITHIOSULFITES, $(CH_3)_3CSS(O)SR$ (100°)

R	$t_{1/2}$, hr	Yield of SO_2, %	λ_{SO}, cm^{-1}
2-Naphthyl[a]	0.25	91	1120
Cyclohexyl	0.25	65	1110
2-Acetamidoethyl	0.25	37	1110

[a] Used after recrystallization from CCl_4–pentane (1:4), mp 70–71°.

The stabilities of two of the unsymmetrical dithiosulfites are intermediate between the stabilities of the corresponding symmetrical ones, but, interestingly, *t*-butyl 2-naphthyl dithiosulfite is less stable than either *t*-butyl or 2-naphthyl dithiosulfite.

Five typical dithiosulfites were synthesized by the method used for **1**; these are shown in Table III in order of decreasing stability. The choice of the five was determined by the effort to obtain substances as low in the stabilities reflected in Tables I and II as seemed feasible. It will be noted that *t*-butyl 2-naphthyl dithiosulfite (**7**) had $t_{1/2}$ as low as 0.25 hr; presumably dithiosulfites with equal or greater $t_{1/2}$ might be isolable.

Because further understanding of the decomposition could suggest additional isolable dithiosulfites, and because of interest in the decomposition itself, kinetic studies were undertaken. The phenyl ester (**4**) was used because of its intermediate stability.

The study was begun with solutions of the phenyl ester (**4**) in carbon tetrachloride in sealed ampoules. A marked autocatalytic effect resulted from sulfur dioxide formed. When sulfur dioxide was removed as formed, reasonably good agreement with first-order kinetics resulted; Figure 1 shows first-order curves thus obtained for the decomposition of ester **4**. Figure 1 (curve C) also makes clear the strongly accelerative effect of sulfur dioxide. Progress of the reaction was followed by the decrease in infrared absorbance of the SO band at 1125 cm^{-1}; the concentration of **4** was determined by comparing these absorbances with a standard curve.

Decomposition of the dithiosulfite **2** also is first order.[4c] It has other features common with those of **1**, notably formation of sulfur dioxide. Evidently the over-all decomposition of the heterocyclic **2** and the acyclic phenyl ester **4** differ, however, because sulfur is formed with **2** but has never been observed with **4** or our other dithiosulfites; furthermore, trisulfides evidently did not form from **2**.[4c]

TABLE III

PURE DITHIOSULFITES PREPARED

No.	R of $(RS)_2SO$	Yield %	Yield Mp, °C	Mp (pure), °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found	S, % Calcd	S, % Found
1	*t*-Butyl	92	48–49.5	51–51.5[a]	42.44	42.57	8.01	7.65	42.49	42.22
3	2-Naphthyl	30[b]	112–114	121–122[c]	65.54	65.57	3.85	3.75	26.25	26.42
4	Phenyl	45[d]	39–40[d]	39.5–40	54.10	54.17	3.78	3.73	36.11	35.89
5	*p*-Methoxyphenyl	77	99–101	101–101.5	51.51	51.30	4.32	4.22	29.47	28.85[e]
6	*o*-Methoxyphenyl	37	90–91[f]	91–91.5	51.51	51.49	4.32	4.35	29.47	29.76
7	2-Naphthyl, *t*-butyl	96	67–69	70–71[g]	56.71	57.03	5.44	5.32	32.45	32.51

[a] After chromatography of 1 g on 30 g of Florisil using hexane, and recrystallization from *n*-pentane; over-all yield, 27%. The nmr spectrum showed only a singlet at τ 8.50. Lit.[4a] mp 46–50°. [b] Prepared in methylene chloride. [c] After chromatography of the crude product on silica gel with 1:1 $CHCl_3$–CCl_4; over-all yield, 10%. [d] After recrystallization from 1:10 CCl_4–pentane. [e] Close checks on two C–H analyses and difficulties with S analyses of other dithiosulfites in this table strongly indicate that the low per cent of S reflects analytical difficulty, not impurity. [f] After recrystallization from 1:5 CH_2Cl_2–pentane. [g] The nmr spectrum showed a singlet at τ 8.5 and a multiplet centered at 2.3; the ratio of aliphatic/ring protons was 1.27 (calcd 1.29).

Disproportionation of ester **4** according to eq 3 is a mechanistic possibility for decomposition but would involve a second-order process.

$$2(RS)_2SO \longrightarrow [(RS)_2SO_2] + RSSSR \qquad (3)$$

$$\downarrow$$

$$RSSR + SO_2$$

Another possibility is a rate-determining extrusion of sulfur monoxide, and its rapid reduction of a molecule of dithiosulfite (eq 4 and 5). A test could be that an unstable dithiosulfite might reduce a stable one if decomposed in its presence. Products should be the disulfide from the unstable dithiosulfite (eq 4) and the trisulfide from the stable one (eq 5), When ester **4** was added to molten *t*-butyl dithiosulfite (**1**), a ratio of 18:1 of *t*-butyl trisulfide to *t*-butyl disulfide was observed, indicating considerable reduction of **1** by an intermediate involved in the decomposition of the phenyl ester **4**. If the reaction shown by eq 4 were strictly concerted, no unsymmetrical sulfides (RSSR′ or RSSSR′) should be formed, beyond trace amounts expected from the disproportionation shown by eq 6.

$$(RS)_2SO \xrightarrow{\text{slow}} (RS)_2 + SO \qquad (4)$$

$$\text{(fast)} \downarrow (RS)_2SO$$

$$(RS)_2S + SO_2 \qquad (5)$$

$$RSSR + R'SSR' \rightleftharpoons 2RSSR' \qquad (6)$$

However, *t*-butyl phenyl disulfide was observed in amounts 15–28 times greater than could be demonstrated to result from simple disproportionation (eq 6) of the sulfides under the same conditions, suggesting that an acceptable mechanism for decomposition must explain intermolecular scrambling of groups. Scrambling was confirmed by analysis of the decomposition products of *t*-butyl 2-naphthyl dithiosulfite (**7**); appreciable quantities resulted of *t*-butyl di- and trisulfide, as well as of 2-naphthyl disulfide (and probably 2-naphthyl trisulfide).

Sulfur monoxide was invoked as an intermediate in the decomposition of **2**, and formation of sulfur with **2** was attributed partially to its disproportionation.[4c] The apparent absence of sulfur in all of the decompositions we have studied, taken with scrambling of groups and formation of trisulfides, suggests that in the present instances simple extrusion of *free* sulfur monoxide is unlikely.

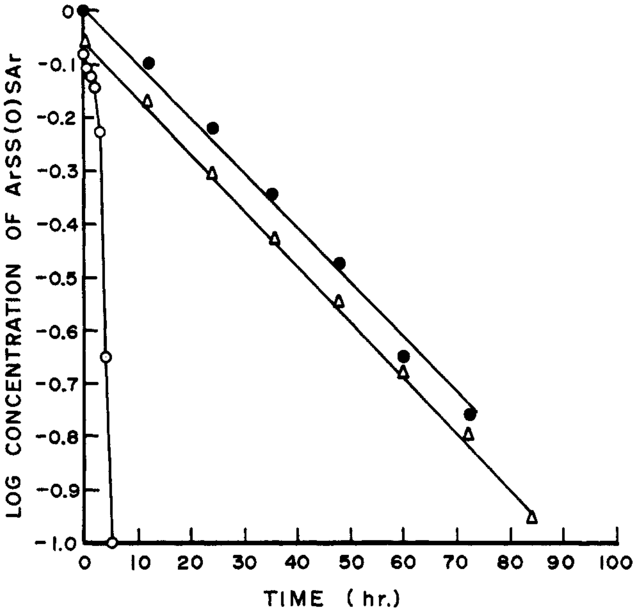


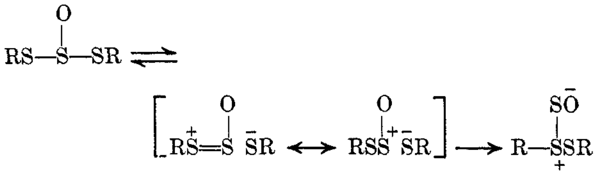
Figure 1.—First-order rate plot for the decomposition of phenyl dithiosulfite (**4**) in refluxing carbon tetrachloride: (a) ●, 1.0 *M*; (b) △, 0.85 *M*; (c) ○, shows the decomposition in the presence of sulfur dioxide.

In a test for possible homolytic character of its decomposition, ester **4** was irradiated in carbon tetrachloride. Infrared spectra before and after irradiation were congruent both for the sample and for a shielded control; hence no appreciable decomposition occurred. The decomposition accordingly seems more likely to be heterolytic than homolytic.

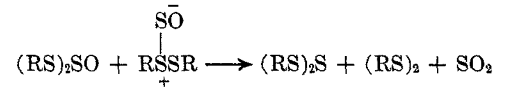
The main points of the decomposition, which must be accounted for by any mechanism, are therefore, as follows. (1) The stoichiometry is that of eq 2. (2) The decomposition is first order, at least for the phenyl ester **4**. (3) Simultaneous decomposition of two dithiosulfites or of an unsymmetrical dithiosulfite results in scrambling of groups. (4) The reaction is induced by heat but not significantly by light. (5) *t*-Alkyl dithiosulfites are far more stable than *sec*-alkyl or primary alkyl dithiosulfites. (6) The decomposition is catalyzed by sulfur dioxide.

The decomposition obviously might be quite complex and a multitude of reactions might be written to explain it. With no intent of proposing a detailed mechanism, and assuming all compounds studied decomposed by the same pattern, we suggest the following as consistent with facts 1–6. Hopefully, these views afford useful correlation of salient points.

First, separation into an ion pair is suggested, followed by a rate-determining rearrangement, resembling internal return, to afford a complex of the disulfide and sulfur monoxide (eq 7). Fast reduction of a second



$$RS\text{—}\overset{O}{\overset{|}{S}}\text{—}SR \rightleftharpoons \left[R\overset{+}{S}=\overset{O}{\overset{|}{S}}\ \bar{S}R \longleftrightarrow RS\overset{O}{\overset{|+-}{S}}SR\right] \longrightarrow R\text{—}\underset{+}{\overset{S\bar{O}}{\overset{|}{S}}}SR \qquad (7)$$

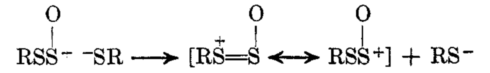


$$(RS)_2SO + R\underset{+}{\overset{S\bar{O}}{\overset{|}{S}}}SR \longrightarrow (RS)_2S + (RS)_2 + SO_2 \qquad (8)$$

molecule of dithiosulfite by the complex could ensue (eq 8). Equations 7 and 8 seem consistent with first-order kinetics and also with stabilization of dithiosulfites by moderately electronegative substituents (*via* inhibition of RS^- in its attack on the other divalent sulfur in eq 7).

This view also conforms to the marked stability of *t*-alkyl dithiosulfites, because attack of the RS^- moiety (when R is *t*-alkyl) on the other divalent sulfur should be sterically difficult. Divalent sulfur substituted with a *t*-butyl group behaves like a neopentyl carbon and an associated steric effect is considered a "neopentyl effect on sulfur."[5] Furthermore, notable stability of unsymmetrical disulfides containing *t*-butyl groups has been attributed to a conformational difficulty involved in bringing two *t*-butyl groups together;[6] an example is that *t*-butyl phenyl disulfide disproportionated to the extent of less than 10% (eq 6) after 336 hr at 100° (see the Experimental Section).

Secondly, an ion pair like that in eq 7 might dissociate to some extent as in eq 9 (*cf.* the rearrangement of



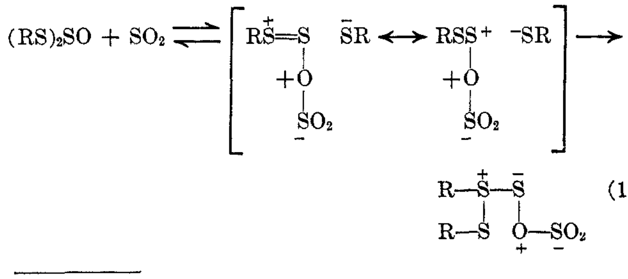
$$RS\overset{O}{\overset{|}{S}}{}^-\ {}^-SR \longrightarrow [R\overset{+}{S}=\overset{O}{\overset{|}{S}} \longleftrightarrow RS\overset{O}{\overset{|}{S}}{}^+] + RS^- \qquad (9)$$

thiocyanates to isothiocyanates).[7] Attack of the thiolate ion on another molecule of dithiosulfite, either to displace another thiolate ion (eq 10) or to be thioalkylated (eq 11), would explain scrambling of groups, although the rate might thereby deviate from first order.

$$(RS)_2SO + R'S^- \rightleftharpoons RSS(O)SR' + RS^- \qquad (10)$$

$$(RS)_2SO + R'S^- \longrightarrow RSSR' + [RSSO]^- \qquad (11)$$

The catalytic effect of sulfur dioxide may be attributed to complex formation between sulfur dioxide and the dithiosulfite (eq 12; only new charges are shown).



$$(RS)_2SO + SO_2 \rightleftharpoons \left[R\overset{+}{S}=\underset{\underset{\underset{-}{SO_2}}{|}}{\underset{+O}{\underset{|}{S}}}\ \bar{S}R \longleftrightarrow RSS^+\underset{\underset{\underset{-}{SO_2}}{|}}{\underset{+O}{}}\ {}^-SR\right] \longrightarrow \begin{array}{l} R\text{—}\overset{+}{S}\text{—}\overset{-}{S} \\ \quad\ |\qquad | \\ R\text{—}S\quad \underset{+}{O}\text{—}\underset{-}{SO_2} \end{array} \qquad (12)$$

Such complexation should accelerate the rate-determining step by increasing the positive character of the still-bonded RS group (and thus its susceptibility to attack by RS^-).

For a detailed, fully defensible mechanism more evidence is necessary, but the difficulty of kinetic studies unfortunately will make it difficultly obtainable (removal of sulfur dioxide at constant temperature without solvent loss, instability of dithiosulfites, etc.).

Several other reactions of dithiosulfites were explored to clarify the chemistry of the class. The reaction with nucleophiles seems to be primarily that of thioalkylation, a result which is not surprising in view of the similarity to well-known thioalkylating agents such as thiolsulfonates (RSO_2SR)[8] and thiolsulfinates [RS(O)SR].[9] Thus reaction of *t*-butyl dithiosulfite (**1**) with thiophenol in the presence of pyridine gave *t*-butyl phenyl disulfide in 67% yield, strongly indicating occurrence of thioalkylation according to eq 11. *t*-Butyl disulfide and *t*-butyl trisulfide were detected in equal amounts (13% of each), presumably in consequence of partial decomposition of the **1** according to eq 2; phenyl disulfide (3%) also was formed. In another experiment, all of the original amount of sulfur was accounted for in organic products; hence sulfur monoxide or sulfur dioxide were not liberated as gases.

The *t*-butyl phenyl disulfide *could* have resulted, however, from an exchange reaction (eq 10), followed by decomposition of the unsymmetrical dithiosulfite. To show, less equivocally, that thioalkylation reactions can indeed occur, the ester **1** was treated with diethyl sodiomalonate. Glpc analysis and spectra indicated that products were diethyl (*t*-butylthio)malonate (32%), together with diethyl malonate (19%), *t*-butyl disulfide (15%), and *t*-butyl trisulfide (34%).

Table I contains only one dithiosulfite which bears a strongly electronegative substituent (*o*-nitro). As mentioned above, no evidence at all was obtained for aryl dithiosulfites with *p*-nitro, tetrafluoro, or ammonium substituents. Inability to obtain these dithiosulfites may well reflect difficulty in synthesis rather than inherent instability. For example, the dithiosulfite may have been destroyed by too facile a thioalkylation of thiol (eq 11); all thiol was consumed and the product appeared (infrared spectrum, melting point) to be impure disulfide.

Saponification of ester **1** resulted in consumption of 1 equiv of alkali. Glpc analysis of the products showed *t*-butyl trisulfide and *t*-butyl disulfide in a ratio of 61:39, implying that part of the **1** is reduced to the trisulfide by a species produced during saponification (*e.g.*, RSSOH, its salt, etc.) in a reaction reminiscent of eq 5; a high ratio of tri- to disulfide in the malonate alkylation may be explained this way also.

Reaction of ester **1** with phenylmagnesium bromide led to six products. Since the reaction obviously was not a clean one, it was not studied further.

It has been claimed that dithiosulfites are easily oxidized in air to the corresponding esters of dithiosulfuric acid.[4a] Samples of dithiosulfites (notably **1**) exposed to the atmosphere for several months (and to a

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[5] For leading references and an example see T. F. Parsons, J. D. Buckman, D. E. Pearson, and L. Field, *J. Org. Chem.*, **30**, 1923 (1965).

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

[7] A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Am. Chem. Soc.*, **87**, 1045 (1965).

[8] For example, see J. C. A. Chivers and S. Smiles, *J. Chem. Soc.*, 697 (1928).

[9] (a) L. D. Small, J. H. Bailey, and C. J. Cavallito, *J. Am. Chem. Soc.*, **71**, 3565 (1949); (b) C. J. Cavallito, J. S. Buck, and C. M. Suter, *ibid.*, **66**, 1952 (1944).

pure oxygen atmosphere for up to 2 weeks) failed to show any evidence of conversion to dithiosulfates. In addition, attempts to oxidize 1 with potassium permanganate in acetone or with hydrogen peroxide in dioxane either failed to effect any oxidation or totally destroyed the ester.

Experimental Section[10]

Synthesis of Pure Dithiosulfites.—Results are given in Table III. Except for 1 (colorless), all compounds were pale yellow (*i.e.*, 3–7); all were recrystallized to constant melting point. All of the dithiosulfites could be kept for many weeks in Dry Ice but most decomposed significantly in a few days at 25° (except 1).

A. **Symmetrical.**[11]—A solution of thiol (20 mmoles) and pyridine (20 mmoles) in ether (50 ml) was added dropwise during 0.25–0.50 hr to a cold (0°), stirred solution of thionyl chloride (10 mmoles) in ether (50 ml). The reaction mixture was stirred at 0° for 0.25–0.50 hr after the addition was completed. It was then transferred to a separatory funnel, washed with two 25-ml portions of ice–water, two 25-ml portions of 1 *N* sodium hydroxide, and with 25-ml portions of ice-water until neutral to pHydrion paper. The organic phase was separated, dried, and evaporated to a residue, which was used directly in the stability studies or purified further to provide analytical samples. Recrystallization from *n*-pentane or a mixture of *n*-pentane and either carbon tetrachloride or methylene chloride usually was effective for purification, although chromatography on Florisil or silica gel was sometimes helpful; it is noteworthy that chromatography on silica gel (Woelm, activity I) with 1:1 chloroform–carbon tetrachloride gave a nearly transparent column in which bands can be followed visually; *this technique may have general applicability and warrants trial by others.*

B. **Unsymmetrical.**—A solution of *t*-butyl mercaptan (10 mmoles) and pyridine (10 mmoles) in ether (30 ml) was added dropwise during 0.25–0.50 hr to a stirred solution of thionyl chloride (10 mmoles) at room temperature.[12] The mixture was stirred for an additional 0.5 hr after the addition was completed. The second thiol (10 mmoles) in ether (30 ml) then was added dropwise during 0.5 hr and the reaction mixture was stirred for an additional 0.25 hr. Isolation of the crude dithiosulfite was effected as in A.

Earlier, when the synthesis was stopped after the addition of *t*-butyl mercaptan and the reaction mixture was shaken with water, the intermediate acid chloride, $(CH_3)_3CSS(O)Cl$, was hydrolyzed to the thiol (shown, after extraction, by iodometric titration). Only a trace of 1, the necessarily alternative product was formed. This result indicated that $(CH_3)_3CSS(O)Cl$ was indeed an intermediate that could be utilized.

An attempt to prepare *t*-butyl 2-naphthyl dithiosulfite (7) by reversing the order of addition of the thiols (at 25°), *i.e.*, by using $2\text{-}C_{10}H_7SS(O)Cl$ as an intermediate, gave 7 in only 5% yield. The major product was 3 in 82% yield.

Decomposition Products of Dithiosulfites. A. *t*-Butyl Dithiosulfite (1).—The ester 1 was essentially undecomposed after 44 hr at 100° (spectrum, melting point) but was decomposed entirely in 8 hr at 150° or 1 hr at 185° (no absorption at 1110 cm^{-1}). To determine the products, 16.94 g (75 mmoles) of 1 was heated at 185° for *ca.* 1 hr in a nitrogen stream, which then was passed through a condenser and Dry Ice trap to 100 ml of 1.0 *N* aqueous alkali.

For identification of sulfur dioxide, the Dry Ice trap was closed off from the reaction flask, and the 2–3 ml of liquid present was distilled at 25° into the alkali; a small sample of the solution with sodium nitroprusside–zinc ferrocyanide gave the blood-red color characteristic of sulfite ion.[13] In another experiment, the boiling point of the liquid was found to be −10° (SO_2, bp −10°); infrared spectra proved this liquid to be sulfur dioxide containing a trace of isobutylene. For determination of sulfur dioxide, the alkaline solution (10 ml) was treated with 10 ml of neutralized 37% aqueous formaldehyde solution (to bind bisulfite and prevent bleaching of the indicator) and was titrated (phenolphthalein) with 0.40 *N* hydrochloric acid (16.0–16.1 ml required, amounting to 95–96% of 1 mole of sulfur dioxide for each 2 moles of 1; *cf.* eq 2). Validity of this procedure for determining sulfur dioxide was proved by assaying known samples of sulfur dioxide with an average error of *ca.* 1%.

In identification of *t*-butyl di- and trisulfide, the residual oil in the original reaction flask (13.9 g, 96% of the weight expected by eq 2 for the equimolar mixture of di- and trisulfide) proved to have an infrared spectrum congruent with that of authentic *t*-butyl disulfide (that of the *t*-butyl trisulfide is virtually identical). Glpc analysis (column, 150°; flow rate, 60 ml/min) showed two (only) components present in about 1:1 ratio, the more volatile of which had a V_r (87 ml) identical with that of authentic *t*-butyl disulfide (peak enhanced by authentic sample); the V_r of the second component (*t*-butyl trisulfide) was 170 ml.

The remainder of the 13.9 g of residue was fractionally distilled using a 20-cm spinning-band column. As a result, two, pure (glpc) components were isolated: (a) 2.60 g (39% yield), bp 68–70° (8 mm), $n^{20}D$ 1.4923; the nmr spectrum showed a singlet at τ 8.65 [for *t*-butyl disulfide lit.[14] bp 64° (5.5 mm), $n^{20}D$ 1.4921]; (b) intermediate fractions (di- and trisulfide) totaling 3.90 g were followed by a second pure component of 5.5 g (70%), bp 92° (2 mm), $n^{20}D$ 1.5224; the nmr spectrum showed a singlet at τ 8.55; mp 16–17° [for *t*-butyl trisulfide lit.[14] bp 85–87.5° (5 mm), $n^{20}D$ 1.5225, mp 17°].

Anal. Calcd for $C_8H_{18}S_3$: C, 45.66; H, 8.62; S, 45.72. Found: C, 45.67; H, 8.61; S, 45.58.

Residue after the distillation weighed 0.90 g, making a recovery of 93%.

To determine rigorously the relative amounts of di- and trisulfide produced, a 50% solution of 1 in *n*-pentane was subjected to pyrolytic conditions on a glpc column. At 150° (flow rate, 150 ml/min), three peaks in addition to solvent resulted. The first two were identified as *t*-butyl di- and trisulfide by adding authentic samples (obtained as above) and observing peak enlargement; the third was believed to be the dithiosulfite 1. As the column temperature was increased, a small fourth peak was observed at 200° (probably *t*-butyl tetrasulfide). The results are summarized in Table IV.

TABLE IV

Identity	Relative amounts at column temp shown, °C					
	150	160	180	200	210	220
t-Butyl disulfide	10	18	39	42	47	48
t-Butyl trisulfide	10	17	44	48	48	48
t-Butyl dithiosulfite	80	55	17	5	0	0
t-Butyl tetrasulfide	0	0	0	5	5	4

B. **Phenyl Dithiosulfite** (4).—Crude 4 (*ca.* 22 g) was heated at 100° for 5 hr in a stream of nitrogen, which was passed through 50 ml of 1.0 *N* sodium hydroxide as in A; aliquots were mixed with formalin and were titrated with acid. The results indicated that 32.8 mmoles of sulfur dioxide was trapped (80% of that calculated by eq 2). The residue was 19.10 g of partially crystalline material which, washed with cold pentane and recrystallized, gave 8.60 g (95%) of phenyl disulfide, mp and mmp 60–61°. Attempted separation of crystalline phenyl trisulfide failed, probably because of its low melting point (30°)[14] and impurities introduced by partial disproportionation of the trisulfide.

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[10] Melting points are corrected. Analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Nmr spectra were done using a Varian Model A-60 spectrometer; purchase of this instrument was made possible by a generous grant from the National Science Foundation. Infrared spectra were obtained using a Perkin-Elmer Model 137B or a Beckman Model IR 10 spectrophotometer. Gas–liquid partition chromatographic (glpc) analyses were effected using an F and M Model 720 chromatograph as follows: carrier gas, helium; column, 2-ft stainless steel (0.25 in. o.d.) packed with silicone gum rubber (5%) on Chromosorb P; thermal conductivity detector; bridge power, 150 ma; block temperature, 250°; injection-port temperature, 250°; values of per cent from glpc analysis are for per cent area in a given peak with reference to the total area of all peaks (except solvent), equivalent thermal conductivities being assumed. Moist extracts usually were dried over anhydrous magnesium sulfate and solvents then were evaporated under reduced pressure using a rotary evaporator. Unless otherwise noted, reagents were commercial materials purified or dried by usual means.

[11] Modified from the method of W. F. Wolff.[4a]

[12] An attempt to prepare 7 at 0° as in A, gave only 5% of 7; 3 resulted instead (82%).

[13] F. Feigl, "Spot Tests, Inorganic Applications," Vol. I, Elsevier Publishing Co., New York, N. Y., 1954, p 283.

[14] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co. Inc., New York, N. Y., 1960, Chapter 7.

C. Decomposition of Isopropyl and *n*-Butyl Dithiosulfite.—Crude isopropyl dithiosulfite (11.80 g, $n^{25}\text{D}$ 1.5348) had a strong infrared band at 1110 cm^{-1}. Overnight storage at *ca.* 25° resulted in a strong odor of sulfur dioxide and in loss of absorption at 1110 cm^{-1}. The refractive index then was $n^{25}\text{D}$ 1.5195; the average of the indexes of isopropyl disulfide ($n^{25}\text{D}$ 1.4891)[14] and isopropyl trisulfide ($n^{25}\text{D}$ 1.5351)[14] is 1.5121.

Fractional distillation of the residue using a 20-cm spinning-band column gave two products: (a) bp 55–57° (7 mm), $n^{25}\text{D}$ 1.4893; isopropyl disulfide[14] has bp 54–55° (7.5 mm), $n^{25}\text{D}$ 1.4891; (b) after several intermediate fractions, a fraction appeared with bp 88° (7 mm), $n^{25}\text{D}$ 1.5333; isopropyl trisulfide[14] has bp 75–76° (5 mm), $n^{25}\text{D}$ 1.5351. The pot residue showed indication of higher sulfides.

Glpc analysis after attempted synthesis of *n*-butyl dithiosulfite confirmed the presence of *n*-butyl disulfide and what might have been *n*-butyl trisulfide.

Assay of Stability of Dithiosulfites.—The crude dithiosulfite (*ca.* 10 mmoles, weighed precisely), prepared as described in the general procedures, was heated at 100° in a 50-ml, three-necked flask (fitted with a magnetic stirrer, nitrogen-inlet tube, and condenser, and preheated to 100°). Nitrogen was passed through the flask and condenser and then, *via* a capillary, through 10.0 ml of 0.5 *N* aqueous sodium hydroxide solution.

Samples (25–50 ± 0.1 mg) were taken after 0.05, 1, 2, 4, 8 hr, etc., and were diluted using spectroquality carbon tetrachloride (1 ± 0.01 ml/25 mg of sample). The time required for the absorbance of the SO band in the infrared region at 1110–1145 cm^{-1} (determined by the best-baseline procedure) to diminish to one-half of its original value was designated as $t_{1/2}$ (Tables I and II). Sulfur dioxide was determined by titration of excess alkali as described above, and the amount relative to that assuming the sample to have been pure dithiosulfite quantitatively produced and then quantitatively decomposed according to eq 2 is reported in Tables I and II as per cent yield of SO_2.

Kinetics of the Decomposition of Phenyl Dithiosulfite (4). A. In a Closed System.—Approximately 0.5 ml of a solution of **4** in carbon tetrachloride (0.85 *M*) was placed in each of seven 2-ml glass ampoules. The ampoules were sealed and heated in boiling carbon tetrachloride. Ampoules were opened immediately after withdrawal, and the absorbance of the SO band at 1125 cm^{-1} was determined using the best baseline procedure. The concentration of **4** remaining was determined by comparing absorbances with a Beer's law plot prepared from solutions of known concentration of **4**; the Beer's law plot was linear and passed through the origin. Results are shown in curve c of Figure 1.

Marked acceleration of decomposition at 2–3 hr is clear from Figure 1 and indicates the decompositon to be autocatalytic.

B. With Removal of Sulfur Dioxide.—A solution of **4** (35 ml, 0.85 *M*) in carbon tetrachloride (spectroquality) was placed in a 50-ml flask protected from light by a foil wrapping and equipped with a sampling port. The flask was connected to a reflux condenser through a device similar to a Soxhlet extractor but without a siphon arm and with the barrel open to the flask below. The refluxing vapor passed through the side-arm by-pass to the condenser and the condensate then dripped through a thimble containing Ascarite previously equilibrated with carbon tetrachloride and back into the reaction flask (solvent loss during the reaction was minimal). The carbon tetrachloride thus was scrubbed free of sulfur dioxide. The reaction mixture was heated to reflux and samples were withdrawn at 12-hr intervals. As in A, the absorbance was determined and was converted to the concentration of **4** remaining (C_t). A plot of log C_t *vs.* time (Figure 1, curve b) was linear to 86% decomposition, indicating a first-order rate law. By use of the expression $k = (2.303/t)(\log C_0/C_t)$, the average rate constant was calculated to be $6.3 \pm 0.5 \times 10^{-6}$ sec^{-1}. A similar decomposition of a 1.0 *M* solution of **4** gave a first-order plot linear to 83% decomposition (Figure 1, curve a); $k = 6.6 \pm 0.8 \times 10^{-6}$ sec^{-1}. Concentrations were not varied to greater extent because of experimental difficulties.

Decomposition of Phenyl Dithiosulfite (4) in the Presence of *t*-Butyl Dithiosulfite (1).—Dithiosulfite **1** (5.65 g, 25 mmoles, rather stable at 100°, as described above) was heated at 100°. The ester **4** (6.66 g, 25 mmoles) was added portionwise during 2 hr, and the mixture then was kept at 100° for 3 more hr. Infrared absorption in the SO region for both **1** and **4** decreased to about 10% of that of an equivalent amount of an equimolar mixture of the two. Glpc analysis of the reaction mixture (column temperature, 200°; flow rate, 120 ml/min) indicated the following products (in order of elution): *t*-butyl disulfide (1%), *t*-butyl trisulfide (18%), *t*-butyl phenyl disulfide (28%), phenyl disulfide (29%; column A, below; glpc analysis of **4** and its decomposition products indicated that phenyl trisulfide decomposed on the column).

To determine whether phenyl di- and trisulfide could cause *t*-butyl trisulfide to dominate over the disulfide, as shown in column A, 1 g of a mixture of phenyl di- and trisulfide from a separate decomposition of **4** was heated for 5 hr with *t*-butyl dithiosulfite at 100°. No significant decomposition of **1** occurred (infrared spectrum). Glpc analysis (**1** decomposes on the column) gave the results in column B, which show only about 6:1 rather than 18:1 domination of *t*-butyl tri- over disulfide; column B also shows scrambling of groups occurred on the glpc column. In a third experiment, the sulfides (1 g) from the decomposition of **4** were mixed with *t*-butyl disulfide (0.38 g) and *t*-butyl trisulfide (0.45 g) and heated at 100° for 5 hr. Results of the glpc analysis (column C) show that no significant formation of *t*-butyl phenyl disulfide occurs according to eq 6 under these conditions (see Table V).

TABLE V

Component	Per cent of total area A	B	C
t-Butyl disulfide	1	4	21
t-Butyl trisulfide	18	23	21
t-Butyl phenyl disulfide	28	15	1
Phenyl disulfide	29	40	54

Decomposition of *t*-Butyl 2-Naphthyl Dithiosulfite (7).—Thin layer chromatography of the products arising from decomposition of **7** (0.5 hr, 100°) on Eastman Chromogram Sheet, Type K 301 R (silica gel), eluted with *n*-hexane and developed in iodine vapor, gave spots with the following R_f values: 0.42 (R_f of *t*-butyl trisulfide, 0.41), 0.36 (R_f of *t*-butyl disulfide, 0.36), 0.24 (presumably the unsymmetrical sulfides), 0.14 (R_f of 2-naphthyl disulfide, 0.14; we suspect that the trisulfide is inseparable), and 0 (R_f of **7**, 0).

Influence of Light on Phenyl Dithiosulfite (4).—The ester **4** in carbon tetrachloride (10 ml, 1 *M*) was chilled in ice and irradiated for 8 hr with a 100-w Hanovia ultraviolet source (heat filter) from a distance of 6 in. An identical control solution was wrapped with foil and was maintained under the same conditions. Infrared spectra in the region of 1200–600 cm^{-1} of the irradiated sample before and after exposure were congruent, as were those of the control, and also of the irradiated sample and the control. It was concluded that little decomposition had occurred.

Reactions of *t*-Butyl Dithiosulfite (1). A. With Thiophenol.—No appreciable reaction occurs between **1** and thiophenol alone and very little between **1** and pyridine, even under forcing conditions. In the reaction of all three together, separate solutions of **1** (4.52 g, 20 mmoles), of thiophenol (4.40 g, 40 mmoles), and of pyridine (3.16 g, 40 mmoles) were prepared in 10 ml of spectroquality carbon tetrachloride. The mixture was kept under nitrogen and protected from light for 3 days. An infrared spectrum then indicated that only 12% of **1** remained. Glpc analysis (column temperature, 175°; flow rate 60 ml/min) showed five peaks. Four were identified by peak enhancement with authentic samples. The components, in order of elution, were: *t*-butyl disulfide (13%), *t*-butyl trisulfide (13%), *t*-butyl phenyl disulfide (67%), unknown (3%), and phenyl disulfide (3%).

The remainder of the reaction mixture was washed free of pyridine with 1 *N* hydrochloric acid. Unreacted thiol (undetected in glpc analysis because V_r was the same as that of solvent) was extracted with 3 *N* aqueous alkali (acidification and iodine titration showed that 15% of the thiol remained). Distillation of the neutral products using a 20-cm spinning-band column gave (assuming no aliquots had been removed) 2.6 g (39%)[15] of *t*-butyl phenyl disulfide, bp 98–102° (2 mm), $n^{25}\text{D}$ 1.5680. The infrared spectrum was congruent with that of the authentic disulfide described below.

The fate of the oxygen atom of the SO moiety and the question of whether volatile sulfur oxides or soluble inorganic sulfur compounds (sulfide, sulfite, etc.) were formed was of special interest.

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[15] Assuming that 1 mole of **1** reacts with 2 of thiol to give 2 of disulfide, and based on thiol actually consumed (34 mmoles).

To determine the sulfur balance, a mixture of 1 (4.52 g, 20 mmoles), pyridine (3.16 g, 40 mmoles), and thiophenol (8.80 g, 80 mmoles) in carbon tetrachloride (50 ml) was allowed to react as before. The reaction mixture, washed with water and acid, was dried and evaporated to 13.0 g of oil. Analysis of the residue showed the sulfur content to be 34.86% or 4.53 g, showing the total recovery of sulfur (original amount, 4.49 g) as organic sulfur compounds to be 101%.

B. **Synthesis of Authentic *t*-Butyl Phenyl Disulfide.**—*t*-Butylsulfenyl chloride was prepared by allowing 7.5 g (106 mmoles) of chlorine to distil into a stirred solution of *t*-butyl disulfide (18.9 g, 107 mmoles) in *n*-pentane (200 ml) during 0.5 hr at 25–28°.[16] The mixture was stirred for 0.5 hr and then was added dropwise (1 hr) to a stirred solution of thiophenol (23.3 g, 212 mmoles) and dry pyridine (16.8 g, 212 mmoles) in *n*-pentane (250 ml) at 0°. The reaction mixture was stirred for 0.25 hr after the addition of the sulfenyl chloride was completed and then was washed with water, acid, aqueous alkali, and again with water until neutral. Drying, concentration, and distillation using a 20-cm spinning-band column gave 23.0 g (55%) of *t*-butyl phenyl disulfide, bp 87° (1 mm), $n^{25}{}_{\mathrm{D}}$ 1.5710; the infrared spectrum was identical with that of material isolated earlier.[5]

Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11; S, 32.33. Found: C, 60.65; H, 7.09; S, 32.04.

In a study of the disproportionation (eq 6) of *t*-butyl phenyl disulfide, a solution of 0.4968 and 0.3355 g of durene was prepared in sufficient 95% ethanol to give 25.0 ml. One milliliter of this solution was placed in each of 20 ampoules, which then were sealed. Half of the ampoules were shielded against light, and all were heated in boiling water. Samples were withdrawn at times up to 336 hr, at which point glpc analysis showed that the ratio of the area of the disulfide peak to that of the durene peak remained constant at 1.42 ± 10%, with no appreciable difference between shielded and unshielded samples. Furthermore, no trace of *t*-butyl disulfide could be detected. The extent of disproportionation of *t*-butyl phenyl disulfide after 336 hr therefore was less than 10% (estimated range of experimental error).

C. **With Diethyl Malonate.**—Sodium metal (2.30 g, 100 mg-atoms) was dissolved in absolute ethanol (100 ml). Diethyl malonate (8.00 g, 50 mmoles) and 1 (11.30 g, 50 mmoles) were added and the mixture was heated at reflux for 3 hr. Water was added, the mixture was neutralized with acid, and a methylene chloride extract was washed, dried, and concentrated to 12.10 g of oil. Glpc analysis (column temperature, 150°; flow rate, 60 ml/min) indicated a complex mixture of diethyl malonate (19%), *t*-butyl disulfide (15%), *t*-butyl trisulfide (34%), and an unknown component (32%) thought to be diethyl (*t*-butylthio)-malonate. Two distillations (of the oil) using a 20-cm spinning-band column afforded 0.44 g of material with bp 79–80° (0.05 mm), $n^{25}{}_{\mathrm{D}}$ 1.4837; glpc analysis showed this to consist of 88% of presumed diethyl (*t*-butylthio)malonate. The infrared spectrum was consistent (ester and *t*-butyl groups). The nmr spectrum also was consistent. It showed a CH_3 multiplet centered at τ 8.68 (diethylmalonate, 8.73), the CH_2 quartet of the ethyl groups centered at 5.80 (diethyl malonate, τ 5.78), and a singlet at 5.96 (the multiplet for the methinyl hydrogen of diethyl methylmalonate is centered at τ 6.65 and the methylene singlet of diethyl malonate occurs at 6.63). Thus the nmr spectrum indicated the major component of the mixture to be a monosubstituted diethyl malonate in which the methinyl hydrogen was significantly deshielded by the *t*-butylthio substituent.

It is concluded that thioalkylation occurs with diethyl sodiomalonate just as with thiophenol and that a major product of this reaction is diethyl (*t*-butylthio)malonate. Unfortunately, other components in the mixture had too nearly the same boiling point to permit a facile separation, and the reaction clearly has negligible preparative value in its present form.

D. **Saponification.**—Methanolic potassium hydroxide (25.0 ml, 0.82 *N*) was heated with 0.7982 g (3.53 mmoles) of 1 under reflux for 0.25 hr. Neutralized formaldehyde solution (5 ml of 37% solution) was added to the cooled mixture, which then was titrated with acid. The saponification equivalent was 216 (a second experiment gave 235) (mol wt of 1, 226). Extraction with pentane and glpc analysis showed that the products consisted of *t*-butyl trisulfide (61%) and *t*-butyl disulfide (39%).

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The Mechanism of the Disproportionation of Sulfinic Acids. Rate and Equilibrium Constants for the Sulfinic Acid–Sulfinyl Sulfone (Sulfinic Anhydride) Equilibrium[1]

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Using spectrophotometric techniques it has been possible to measure in acetic acid–water solvent both the rate and equilibrium constants associated with the equilibrium between *p*-toluenesulfinic acid (Ia) and *p*-toluenesulfinyl *p*-tolyl sulfone (IIa). Such data are of interest because of the role of the sulfinyl sulfone as an intermediate in the disproportionation of Ia. While the present results unequivocally confirm the mechanism proposed earlier for the disproportionation reaction, they also reveal several important and previously unrealized complexities associated with it. Specifically, the rate of hydrolysis of IIa to sulfinic acid is found to be much more closely comparable with the rate of thermal decomposition of IIa than had previously been imagined, particularly at high temperatures and low acidities. This means that thermal decomposition of IIa is not always the rate-determining step in the disproportionation reaction. One also finds that at low acidities extremely small concentrations (10^{-4} *M*) of added potassium chloride can rather dramatically accelerate the rate of attainment of equilibrium between Ia and IIa. Since chloride ion is very likely a common impurity in inadequately purified samples of sulfinic acid, this introduces further potential complications into interpretation of kinetic data for the disproportionation reaction.

Previous studies[2-4] of the disproportionation of aromatic sulfinic acids (eq 1) have suggested that the mechanism of the reaction is as outlined in Chart I.

$$3ArSO_2H \longrightarrow ArSO_2SAr + ArSO_3H + H_2O \qquad (1)$$

This involves an initial equilibrium (eq 2) between the sulfinic acid and an unstable sulfinyl sulfone (II), followed by unimolecular thermal decomposition of II (eq 3). The latter reaction is apparently[3] a homolytic dissociation of the sulfur–sulfur bond in II, with subsequent head-to-tail recombination of the radical fragments giving the sulfenyl sulfonate III. Reaction of III with an additional molecule of sulfinic acid (eq 4) yields the final products.

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