The progress of the rearrangement could be followed easily by the shift of the carbonyl absorption in the infrared spectrum from the thiol ester position (5.95 μ in the case of the acetate esters) to the amide position at about 6.15 μ. In most cases the amide was isolated by direct distillation, the polythioformaldehyde remaining undistilled, m.p. 185–190°.[15] The infrared and n.m.r. spectra of the latter were identical with those of an authentic sample.

Organic Disulfides and Related Substances. XIV. Aspects of the Reaction of Thiolsulfonates with Thiols[1a,c]

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In the presence of base, a typical thiolsulfonate reacts readily and completely with a thiol to form a disulfide and a sulfinic acid salt even at −86°. In the absence of base, fairly rapid reaction occurs, which proceeds only part way, but can be pushed toward completion by use of excess thiol or thiolsulfonate. Steric factors significantly affect reactivity of thiolsulfonates, more so than do electronic effects noted thus far. As ancillary points, gas–liquid chromatography was investigated for qualitative and quantitative analysis of thiols, and a tertiary alkyl thiolsulfonate was synthesized, apparently for the first time.

The reaction of thiolsulfonates with thiols has provided a route to disulfides, which has been little exploited[2] and about which little is known except that it occurs readily even at 0°.[3] The principal reaction is formulated in eq. 1 and important subsidiary reactions in eq. 2 and 3. Having found recently that the reaction provides a clean and useful synthesis for many types of disulfides,[4–8] we felt attention to its characteristics was well warranted.

$$R_1SO_2SR_2 + R_3SH \longrightarrow R_1SO_2H + R_2SSR_3 \quad (1)$$

$$3R_1SO_2H \longrightarrow R_1SO_2SR_1 + R_1SO_3H + H_2O \quad (2)$$

$$2R_2SSR_3 \rightleftharpoons R_2SSR_2 + R_3SSR_3 \quad (3)$$

Of several techniques considered for following the reaction,[1b] only two proved promising in practice. These led to useful conclusions, although unhappily they were not adaptable to detailed kinetic work. The first technique was the potentiometric determination of sulfinic acid formed (eq. 1), using as the end point a rather sharp break found for sulfinic acids (*e.g.*, *p*-toluenesulfinic acid) at pH 5.5–7.5; it was hoped that thiol would not interfere since many thiols (*e.g.*, *p*-toluenethiol) are neutralized only at about pH 9.5–10.5. Barnard and Cole quantitatively determined thiolsulfonates essentially in this way, allowing them to react with excess thiol and titrating the sulfinic acid formed.[9]

The data obtained, puzzling at first, soon showed the inadequacy of titration for studying the kinetics of eq. 1. One difficulty was the very short survival time sometimes observed for the sulfinic acid. Kice and coworkers have shown both that sulfinic acids themselves decompose by complex mechanisms and that they may react with species such as disulfides present in our system.[10] Equation 2 suggests disproportionation as a principal cause of loss.

When *p*-tolyl *p*-toluenethiolsulfonate reacted at 0° with *p*-toluenethiol, *p*-toluenesulfinic acid which formed survived quite well. For example, titration after 4 min. required 101% of one molar proportion of alkali and after 5–72 hr. the result was virtually the same; at −86°, 93% resulted after 4 min. and change again was negligible after many hours. In marked contrast, 2-mercaptoethylamine hydrochloride (**1**), a thiol of special interest to us, resulted at 0° in 70% of sulfinic acid after 2 min. but in only 12% after 2 hr., obviously because the sulfinic acid began to be destroyed soon after formation; at −86°, 80% was found after 2 min. but only 55% after 1.5 hr. Addition of pyridine in the hope of stabilizing *p*-toluenesulfinic acid as its pyridine salt at −8° caused eq. 3 to become more important, and cystamine dihydrochloride resulted in 65% yield.

A second and even more serious difficulty was that the titration itself affected the reaction. The yields of 80–93% of sulfinic acid rapidly produced even at −86° implied that the reaction was fast and complete. At odds with this conclusion is the recovery of 25% of *p*-toluenethiol after its reaction with 2-aminoethyl 2-aminoethanethiolsulfonate dihydrochloride (**2**).[4] The explanation for the paradox is that alkali titration must actually produce enough thiolate ion to drive the reaction toward completion. Rather good yields of aminodisulfide hydrochlorides found in our synthetic applications of the reaction no doubt have this explanation also—alkali intended only to convert aminodisulfide hydrochloride products to free bases in isolations actually no doubt functioned also to form thiolate ions and thus to force the thiolsulfonate reactions toward completion[4,6–8]; in substantiation, when thiols have been extracted before addition of alkali, recoveries of thiol have been about 50%.[1b]

(1) (a) This investigation was supported by the U. S. Army Medical Research and Development Command, Department of the Army, under Research Contract No. DA-49-193-MD-2030. Results are abstracted from portions of the Ph.D. Dissertation of T. F. P.[1b] and that forthcoming of J. D. B. (b) T. F. Parsons, Ph.D. Dissertation, Vanderbilt University, May 1964. (c) Paper XIII: L. Field and T. F. Parsons, *J. Org. Chem.*, **30**, 657 (1965). (d) Du Pont Postgraduate Teaching Assistant, 1962–1963. (e) To whom correspondence should be addressed.

(2) *Cf.* A. Schöberl and A. Wagner, "Methoden der Organischen Chemie (Houben–Weyl)," Vol. 9, E. Müller, Ed., 4th Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 72.

(3) H. Gilman, L. E. Smith, and H. H. Parker, *J. Am. Chem. Soc.*, **47**, 851 (1925).

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

(5) R. R. Crenshaw and T. C. Owen, *Proc. Chem. Soc.*, 250 (1961).

(6) L. Field, H. Härle, T. C. Owen, and A. Ferretti, *J. Org. Chem.*, **29**, 1632 (1964).

(7) L. Field, A. Ferretti, and T. C. Owen, *ibid.*, **29**, 2378 (1964).

(8) R. R. Crenshaw and L. Field, *ibid.*, **30**, 175 (1965).

(9) D. Barnard and E. R. Cole, *Anal. Chim. Acta*, **20**, 540 (1959).

(10) *Cf.* J. L. Kice and N. E. Pawlowski, *J. Org. Chem.*, **28**, 1162 (1963), and references cited therein; J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605, 2384, 2390 (1962).

TABLE I

EXTENT OF REACTION OF THIOLSULFONATES ($R_1SO_2SR_2$) WITH BENZENETHIOL[a]

R_1	R_2	Molar proportions: $R_1SO_2SR_2$	C_6H_5SH	Pyridine	Reaction time, hr.	Extent of reaction, %[a]: From C_6H_5SH unconsumed[b]	From $R_1SO_2SR_2$ unconsumed[c]
		A. By Gas Chromatographic Analysis					
C_6H_5	C_6H_5	1	1	0	1[d]	27	
		1	1	1	1[e]	100[e]	
		1	2	0	2[d]	60	
		2	1	0	2[d]	45	
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	1	1	0	2.5[d]	44	
p-ClC_6H_4	p-ClC_6H_4	1	1	0	3[d]	41	
		B. By Larger Scale Isolation					
C_6H_5	C_6H_4	1	1	0	1	31	36
		1	1	1	1	99	
2,4,6-(i-Pr)$_3C_6H_2$	2,4,6-(i-Pr)$_3C_6H_2$	1	1	0	1	34	32
		1	1	1	1	49	
p-$CH_3C_6H_4$	$(CH_3)_3C$	1	1	1	1	45	49
		1	1	1	3	44	45
		1	1	1	48	72	92
		1	1	1	192	72	
		1	1	3	1.5	92	
		1	1	3	20	92	

[a] Based on the equation $R_1SO_2SR_2 + C_6H_5SH \rightarrow R_1SO_2H + C_6H_5SSR_2$. [b] Determined in gas-chromatographic experiments by ratios of thiol peak heights and in larger scale isolation by distillation and titration. [c] Isolated by recrystallization and identified by mixture melting point and/or infrared spectrum. [d] Approximate time at which the *maximum* amount of benzenethiol had been consumed. Up to this point thiol was still disappearing; after it the benzenethiol peak no longer decreased (and indeed seemed to increase slightly). [e] Increase in the thiol peak as mentioned in footnote *d* did not occur.

Because of the difficulties mentioned with titration, a second analytical method was resorted to—that of gas–liquid chromatography. This method, it should be added, was promising as a general analytical tool for thiols—its value for qualitative analysis was shown by quite different retention times for typical thiols, and for quantitative analysis by linear correlations of peak heights with concentration.

Other species of the reaction were tested singly and combined and were found not to interfere with the gas-chromatographic determination of benzenethiol (benzenesulfinic acid, phenyl disulfide, phenyl benzenethiolsulfonate); under the conditions used, they did not emerge from the column and did not produce benzenethiol.

Reactions of several thiolsulfonates were studied with benzenethiol. The results are summarized in Table IA. Contrary to implications from the titration experiments, chromatography revealed that little thiol was consumed. Thus after 1 hr. only 27% of the benzenethiol used had reacted with phenyl benzenethiolsulfonate and the reaction had come to a standstill. When a molar proportion of pyridine was added, benzenethiol consumption was 100% after 1 hr., no doubt because of the greater proportion of more nucleophilic thiolate ion.

When phenyl disulfide was treated with benzenesulfinic acid under various conditions (including trial of thiol or thiolsulfonate as catalysts), no significant amounts of benzenethiol were detected. The reaction thus seems irreversible. Nonetheless, Table IA shows that for phenyl benzenethiolsulfonate excess thiol or thiolsulfonate results in a more complete reaction (40–65% instead of 27%; furthermore, a 0.5 molar proportion of benzenesulfinic acid slowed reaction of benzenethiol and phenyl benzenethiolsulfonate to about the rate of p-tolyl p-toluenethiolsulfonate). It might be added that Gibson and Loudon found certain other displacements of sulfonyl groups to be reversible (they also mentioned, but only in passing, that mercaptides react rapidly with thiolsulfonates).[11]

Table IA suggests that the benzenethiolsulfonate reacts more rapidly than the p-toluene analog and this in turn more rapidly than the p-chloro. The differences are not startling, however. The p-nitro compound was too sparingly soluble for comparison.

Larger scale isolations verified the conclusions from gas chromatography. These results are summarized in Table IB. After benzenethiol and phenyl benzenethiolsulfonate had reacted for 1 hr., 69% of thiol and 64% of thiolsulfonate were recovered. When a molar proportion of pyridine was added, only 1% of thiol could be detected and phenyl disulfide was isolated in 91% yield.

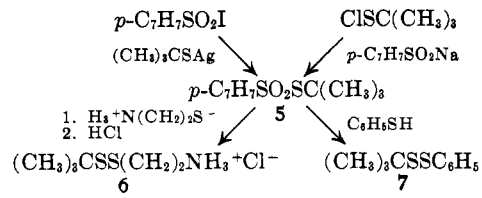
Steric factors were investigated using 2,4,6-triisopropylphenyl 2,4,6-triisopropylbenzenethiolsulfonate (**3**). For confirmation of structure, we treated **3** with the mercaptoethylamine salt **1** to convert it to the disulfide **4**, a procedure previously quite effective

$$\underset{\mathbf{3}}{2,4,6\text{-}(i\text{-}Pr)_3C_6H_2SO_2SC_6H_2\text{-}2,4,6\text{-}(i\text{-}Pr)_3} + \underset{\mathbf{1}}{HS(CH_2)_2NH_3^+Cl^-} \longrightarrow \underset{\mathbf{4}}{2,4,6\text{-}(i\text{-}Pr)_3C_6H_2SS(CH_2)_2NH_3^+Cl^-}$$

for preparing aminoethyl disulfides such as **4**.[6,8] The reaction failed. On the other hand, the zwitterionic free base of **1** was sufficiently nucleophilic to effect 65% conversion of the thiolsulfonate **3** to the disulfide (isolated as its hydrochloride, **4**). The unexpected and atypical failure of **1** to react with **3** suggests clearly that a marked steric effect functions in the reactions of **3** (the failure also again confirms the greater reactivity of a thiolate than of a thiol, as mentioned above).

(11) D. T. Gibson and J. D. Loudon, *J. Chem. Soc.*, 487 (1937).

CHART I



Also of interest sterically was a tertiary alkyl thiolsulfonate, apparently a novel class. *t*-Butyl *p*-toluenethiolsulfonate (**5**) was prepared as shown in Chart I. Its structure is assured by the two independent syntheses shown and by conversion to the known disulfide **6**. Although the route *via* the sulfonyl iodide worked, that *via* the sulfenyl chloride gave purer product in higher yield.[12] Worth emphasis is the resemblance of thiosulfonate **5** to **3** in reacting readily with 2-mercaptoethylamine (67% yield) but not with its hydrochloride (**1**).

The conspicuous resistance of thiolsulfonates **3** and **5** to attack by thiol **1** made it of interest to learn whether attack by the more representative thiol, benzenethiol, would be similarly resisted. Table IB shows that the low reactivity of **3** and **5** does indeed carry over to benzenethiol. Although the isopropylphenyl thiolsulfonate **3** alone reacts about like phenyl benzenethiolsulfonate, in the presence of pyridine the reactions of **3** and **5** with thiophenol were only about half complete in 1 hr., while that of the phenyl ester had been 99% complete; after 48 hr., the reaction of the *t*-butyl ester (**5**) was 72% complete (it could be forced to 92% with more pyridine, which also markedly increased the rate). To assure that eq. 1 actually represented the reaction being studied, the last three reaction mixtures of Table IB were combined and the *t*-butyl phenyl disulfide produced was isolated (59% yield).

The low reactivity of the *t*-butyl thiolsulfonate **5** is qualitatively similar to that shown by *t*-butylsulfenyl compounds as a class toward nucleophilic agents.[13] The reduced reactivity has been ascribed to similarity in the stereochemical requirements for displacement reactions at divalent sulfur and at carbon. Thus the low reactivity of **5** can be understood as another example of the "neopentyl-type" steric effect in sulfur compounds,[13] which here inhibits nucleophilic attack on the divalent sulfur atom. The low reactivity of the triisopropylphenyl thiolsulfonate (**3**) undoubtedly stems from a similar steric shielding (marked hindrance also was seen in the difficult oxidation of the triisopropylphenyl disulfide to the thiolsulfonate **3**).[1c]

Conclusions which seem justified as to the reaction of thiolsulfonates with thiols can be summarized as follows. (1) Bases which will convert a thiol to a thiolate ordinarily cause fast complete reactions, even at −86°. In some circumstances the products will be unstable, the sulfinic acid being lost by eq. 2 and the unsymmetrical disulfide by eq. 3. (2) In the absence of base, a fairly rapid reaction occurs, but apparently proceeds only part way. The reaction does not seem to be reversible, but can be pushed toward completion by excess thiol or thiolsulfonate. (3) Gross differences in reactivity of thiolsulfonates have been associated with steric factors but not yet with electronic ones. Hindered thiolsulfonates will form disulfides with thiols in good yield, but more basic conditions and/or longer reaction times are likely to be necessary.

(12) *Cf.* L. Field, T. F. Parsons, and R. R. Crenshaw, *J. Org. Chem.*, **29**, 918 (1964).

(13) (a) R. G. Hiskey, W. H. Bowers, and D. N. Harpp, *J. Am. Chem. Soc.*, **86**, 2010 (1964); (b) A. Fava and A. Iliceto, *ibid.*, **80**, 3478 (1958); (c) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

Experimental[14]

Reaction of Thiolsulfonates and Thiols. A. With Titration of the Product.—Efforts to follow the reaction by titration of sulfinic acid can be illustrated with a typical experiment. A solution of *p*-toluenethiol (1 mmole) in 95% ethanol (50 ml.) at 0° was added to a similar one of *p*-tolyl *p*-toluenethiolsulfonate. Aliquots were titrated using 0.0611 *N* alkali to a bromophenol blue end point. During 2–30 min. at 0°, various aliquots showed that the percentage of 1 mmole of alkali consumed was 95–101%; it was essentially unchanged during 5–72 hr. subsequently (92–97%).

B. Gas–Liquid Chromatography.—An F and M Model 720 programmed temperature gas chromatograph was used (oven, 125°; detector, 200°; injection port, 175°; flow rate, 50 ml./min.; bridge current, 150 ma.). The column was 2 ft. long and was made of silicone rubber (General Electric Co., SE 30) on Chromosorb W (100–120 mesh); thiol was not detected if a 6-ft. column was used.

Utility of this system for separation of thiols is suggested by the following variations in retention times (sec.): 2-mercaptoethanol, 26; benzenethiol, 56; 2,6-dimethylbenzenethiol, 88; *p*-toluenethiol, 91; α-toluenethiol, 110; *p*-chlorobenzenethiol, 126; and 1-naphthalenethiol, no detection.

Quantitative validity was assured as follows. A solution of durene (9.48 g.) in ethanol (500 ml.) was used to prepare solutions of benzenethiol which were 0.02–0.1 *M*. The thiol solutions (4 μl.) were injected onto the column; constant sample size was assured by constant peak height of the durene internal standard. A plot of peak heights of thiol *vs.* molar concentration was linear and passed through the origin (*i.e.*, zero peak height for zero concentration).

Thiolsulfonates were prepared as described here or earlier.[1c] In an experiment typical of those summarized by Table IA, a solution of 2 mmoles of benzenethiol in 10 ml. of ether was mixed with one of 2 mmoles of phenyl benzenethiolsulfonate at 0°; 0.38 g. of durene also was present. Aliquots were withdrawn at intervals between 3 min. and 4 hr. and injected onto the column. Peak heights of thiol were corrected by multiplying them by the ratio of average durene peak height (through the series) to the height in a given injection. The corrected peak height of thiol then was divided by that found at zero time to determine the percentage of thiol unconsumed. Thiol concentration in this experiment never became less than 73% of the original amount. All experiments in Table IA were done at 0°.

***t*-Butyl *p*-Toluenethiolsulfonate (5). A. Preparation from *t*-Butylsulfenyl Chloride.**[15]—Chlorine (27.5 g., 0.39 mole) was added to a stirred solution of 53 g. (0.30 mole) of *t*-butyl disulfide in 500 ml. of pentane at 27–32° to give *t*-butylsulfenyl chloride.[16] After chlorine addition was complete (*ca.* 1 hr.), the orange solution was stirred 30 min. more and 128 g. (0.6 mole) of sodium *p*-toluenesulfinate dihydrate in 800 ml. of water was added rapidly with ice cooling and vigorous stirring at 15–20°. The mixture was stirred for 2 hr. at *ca.* 25° and then was chilled. Crystalline *t*-butyl *p*-toluenethiolsulfonate (**5**) was removed and recrystallized from ethanol: yield 83 g. (57%), m.p. 68–69°. The melting point was unchanged by further recrystallization from hexane, ethanol, and petroleum ether. The infrared spectrum has the expected strong absorption bands at 815 (*para*-substituted benzene), 1395 and 1365 (*t*-butyl), and 1140 and 1330 cm.$^{-1}$ ($-SO_2-$).

(14) Melting points are corrected. Analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were obtained using a Perkin-Elmer Model 137B Infracord spectrophotometer with Nujol mulls.

(15) Based on analogous reactions of a sulfenyl halide with sulfinate salts by C-P. Lo, H. F. Wilson, and W. J. Croxall, *J. Am. Chem. Soc.*, **76**, 1704 (1954).

(16) W. A. Schulze, G. H. Short, and W. W. Crouch, *Ind. Eng. Chem.*, **42**, 916 (1950).

Anal. Calcd. for $C_{11}H_{16}O_2S_2$: C, 54.08; H, 6.60; S, 26.25. Found: C, 53.94; H, 6.57; S, 25.99.

B. Preparation from *p*-Toluenesulfonyl Iodide.[17]—Silver *t*-butyl mercaptide[18] (3.3 g., 16.7 mmoles) was added slowly to a solution of 4.5 g. (16.0 mmoles) of *p*-toluenesulfonyl iodide[17] in 25 ml. of dry benzene. The suspension was stirred at *ca.* 25° for 30 min. Insoluble material then was removed by filtration and washed with benzene. The combined benzene filtrates were washed twice with 10 ml. of 5% aqueous sodium sulfite and twice with 10 ml. of water and were evaporated under reduced pressure. The amorphous yellow solid left (3.0 g.) was recrystallized from *n*-heptane to give 1.3 g. of thiolsulfonate **5** (34%), m.p. 65–67°, identical with **5** from A (mixture melting point, infrared spectrum).

Reaction of 2-Mercaptoethylamine. A. With the Triisopropylphenyl Thiolsulfonate 3.—Thiolsulfonate **3** (3.0 g., 6 mmoles)[1c] and 2-mercaptoethylamine (0.462 g., 6 mmoles) were stirred in ethanol (250 ml.) for 1 hr. Ethanol was removed, and the residue was suspended in water (150 ml.) and benzene (75 ml.). Iced base (0.40 g. of potassium hydroxide in 30 ml. of water) was added to neutralize the sulfinic acid. The benzene layer was separated, washed with water (100 ml.), and filtered into an iced mixture of 1.7 ml. of 12 *N* hydrochloric acid in 25. ml. of water. Two more benzene extracts of the alkali layer were added to the acid. 2-Aminoethyl 2,4,6-triisopropylphenyl disulfide hydrochloride (**4**) precipitated: m.p. 203–204° dec., yield 1.35 g. (65% conversion; 100% yield based on isolation of 2,4,6-triisopropylphenyl disulfide from the benzene).

Anal. Calcd. for $C_{17}H_{30}ClNS_2$: C, 58.67; H, 8.69; N, 4.03; S, 18.44. Found: C, 58.97; H, 8.72; N, 4.13; S, 18.58.

The attempts to obtain **4** using 2-mercaptoethylamine hydrochloride (**1**) were done using a procedure usually successful for preparing amino disulfides,[4,6-8] *i.e.*, by allowing reaction to occur, then making the mixture alkaline, extracting the free base into organic solvent, and subsequently converting it to the hydrochloride. Only minor conversion to **4** occurred and as much as 74% of thiolsulfonate **3** was recovered.

B. With the *t*-Butyl Thiolsulfonate 5.—A solution of 2.44 g. (10 mmoles) of *t*-butyl *p*-toluenethiolsulfonate (**5**), 1.13 g. (10 mmoles) of 2-mercaptoethylamine hydrochloride (**1**), and 0.56 g. (10 mmoles) of potassium hydroxide in 75 ml. of ethanol was let stand for 3 hr. and then was evaporated under reduced pressure. The residue was dissolved in 25 ml. of water containing 12 mmoles of sodium bicarbonate (to neutralize sulfinic acid) and was extracted with three 25-ml. portions of methylene chloride. The combined organic extracts were washed with 12 mmoles of dilute hydrochloric acid and twice with water. Evaporation of the aqueous extracts under vacuum and washing of the product with absolute ether gave 1.34 g. of 2-(*t*-butyldithio)ethylamine hydrochloride (**6**, 67%), m.p. 195° dec. (lit.[4] m.p. 195° dec.), infrared spectrum identical with that of authentic **6**.[4]

The thiolsulfonate **5** and the thiol salt **1** did not react after 7 days in ethanol (recovery of **5**, 90%). Use of the usual conditions for the reaction[4,6-8] also resulted in only 90% recovery of **5**.

Reaction of Thiolsulfonates with Benzenethiol by Larger Scale Isolation.—The procedure used with phenyl benzenethiolsulfonate also illustrates that used with thiolsulfonates **3** and **5**, as reported in Table IB; all experiments were done at room temperature.

Benzenethiol (1.10 g., 10 mmoles) and 2.50 g. (10 mmoles) of phenyl benzenethiolsulfonate were allowed to react in 25 ml. of dry ether at 25° for 1 hr. Ether and unreacted thiol then were distilled (without heating) at 1 mm. into a Dry Ice chilled trap. Iodine titration of the trap contents showed the presence of 69% of the original benzenethiol. An ether solution of the undistilled residue was washed with aqueous sodium carbonate and evaporated to a solid which, recrystallized, amounted to 1.59 g. of phenyl benzenethiolsulfonate (64% recovery). When 1 molar equiv. of pyridine was used, the undistilled residue proved to be phenyl disulfide, yield (recrystallized) 1.99 g. (91%), m.p. 57–59° (infrared spectrum identical with that of authentic material, m.p. 59–60°); titration of the distillate showed the presence of 1% of benzenethiol.

For isolation of phenyl *t*-butyl disulfide (**7**), the combined undistilled residues from the last three experiments of Table IB were dissolved in ether. The solution was washed with 5% hydrochloric acid and 5% aqueous sodium bicarbonate. Evaporation gave a yellow oil (5.5 g.), which was distilled using a 7 mm. × 21 cm. spinning-band column. The yield of **7** was 3.0 g. (59%, based on benzenethiol consumed); b.p. 106–106.5° (3 mm.), $n^{25}D$ 1.5708, d^{25}_4 1.0408, MD 62.65 (calcd. MD 60.38[19]; exaltation, 2.27).

Anal. Calcd. for $C_{10}H_{14}S_2$: C, 60.56; H, 7.12. Found: C, 60.59; H, 7.10.

(17) Based on the procedures of ref. 12 and of D. T. Gibson, C. J. Miller, and S. Smiles, *J. Chem. Soc.*, **127**, 1821 (1925).

(18) Kindly prepared (*cf.* ref. 17) by W. B. Lacefield. Sodium acetate trihydrate (137 g.) and *t*-butyl mercaptan (90 g.) in water (500 ml.) were added to silver nitrate (170 g.) in water (500 ml.). The precipitate was washed with water, ethanol, and ether, and was dried at 0.1 mm.

(19) Calculated using the value of 7.80 for the atomic refraction of divalent sulfur [W. Strecker and R. Spitaler, *Ber.*, **59**, 1775 (1926)].

Thioureas and Isothiuronium Salts. Monomeric Derivatives

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An attempt has been made to characterize N-vinylthiourea. N-(*p*-Vinylphenyl)thiourea and its N′-methyl- and N′,N′-dimethyl derivatives were prepared. Reaction of the thiourea with methyl iodide afforded S-methyl-N-(*p*-vinylphenyl)isothiuronium iodide and its N′-methyl and N′,N′-dimethyl derivatives, respectively.

As part of a program designed to synthesize potential antiradiation agents, it was decided to prepare polymeric derivatives of thioureas and isothiuronium salts containing structural features similar to S-2-aminoethylisothiuronium bromide hydrobromide (AET) or its propyl analog (APT). Both of these compounds are known to possess radiation-protection properties.[2] The usefulness of a drug is closely related to its rate of excretion and rate of metabolism in the body. Placing the functional groups in a polymeric molecule would be expected to lessen these factors.

The only thioureas reported in the literature containing an unsaturated center are those containing allylic groups. However, owing to chain-transfer properties of such moieties, difficulties are normally encountered in preparing such high molecular weight polymers.

Very few unsaturated derivatives of isothiuronium salts have been reported. Cavallito, *et al.*,[3] prepared benzoylvinylisothiuronium chloride by the addition of thiourea to phenyl ethynyl ketone in the presence of

(1) Taken from a portion of the dissertation submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry, 1964.

(2) J. X. Khym, D. G. Doherty, and R. Shapira, *J. Am. Chem. Soc.*, **80**, 3342 (1958).

(3) C. J. Cavallito, C. M. Martini, and F. C. Nachod, *ibid.*, **73**, 2544 (1951).