Reactions of Thiolsulfonates with Amines

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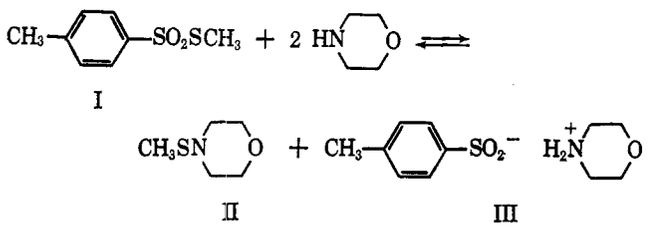
Treatment of alkyl and aryl esters of thiosulfonic acids with primary or secondary amines gave sulfenamides and sulfinic acid salts. Equilibrium constants of several of these reactions were determined. Simple alkyl and aryl thiolsulfonates failed to undergo a detectable reaction with aromatic amines, but *o*-nitrophenyl benzenethiolsulfonate (V) reacted with *p*-anisidine, *p*-toluidine, and aniline in refluxing ethanol. Trichloromethyl *p*-toluenethiolsulfonate (X) and bis(benzenesulfonyl)sulfide (XVIII) were found to react anomalously with morpholine, the former giving *p*-toluenesulfonmorpholide (XI), 4,4′-(thiocarbonyl)dimorpholine (XII), and morpholinium chloride and the latter giving benzenesulfonmorpholide (XIX) and morpholinium benzenethiosulfonate (XX).

Esters of thiosulfonic acids are attacked readily by a variety of nucleophilic agents[1] because of the partially-positive character of the divalent sulfur atom. Other compounds possessing electrophilic divalent sulfur atoms have been reported as reacting with primary and secondary amines to give sulfenamides.[1m,2] This work was undertaken to examine the previously uninvestigated reaction of amines with thiolsulfonates. During the course of our investigation Boldyrev and Kolesnikova[3] reported the reaction in limited scope but with results which were not entirely in accord with our findings.[4]

The reaction of morpholine with methyl *p*-toluenethiolsulfonate (I) in ethyl ether at room temperature gave two products, 4-(methylthio)morpholine (II) and morpholinium *p*-toluenesulfinate (III), which were obtained in 56 and 80%, respectively. The reversibility of the reaction was demonstrated by the reaction of II and III in ethyl ether at room temperature to give the thiolsulfonate (I), which was isolated and identified.



I

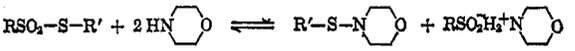
II III

The equilibrium constants (Table I) of the reactions of several alkyl and aryl thiolsulfonates in aqueous acetonitrile were determined by conductimetric measurement of the sulfinate salt products. The results of these determinations show that, as the electronegative character of R′ increases (with accompanying increase of positive character of the divalent sulfur atom), the reaction is facilitated.

The fact that even simple alkyl thiolsulfonates react readily with primary and secondary amines explains why Field and co-workers[5] were unable to isolate thiolsulfonate free bases when neutralizing aqueous solutions of 2-aminoethyl 2-aminoethanethiolsulfonate hydrochloride (IV) with alkali. Since these authors were not successful in isolating any pure product when they allowed thiolsulfonates to react with amines, they suggested that "hydrolytic and not amination reactions are the principal causes of decomposition."

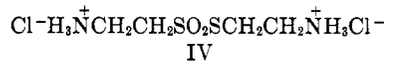
TABLE I

EQUILIBRIUM CONSTANTS[a] OF REACTIONS OF SOME THIOLSULFONATES WITH MORPHOLINE



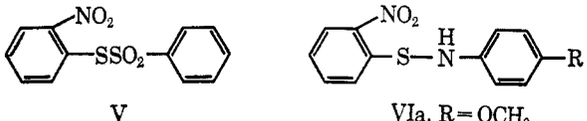
R	R′	K_{equil}
p-$CH_3C_6H_4$	$C(CH_3)_3$	6.1×10^{-3}
p-$CH_3C_6H_4$	CH_3	2.0×10^{-1}
p-$CH_3C_6H_4$	$CH_2CH{=}CH_2$	4.4×10^{-1}
C_6H_5	CH_3	5.4×10^{-1}
C_6H_5	C_6H_5	2.2
C_6H_5	*o*-$NO_2C_6H_4$	27

[a] Determined conductimetrically at room temperature in the solvent system acetonitrile–water (7:1 by volume).

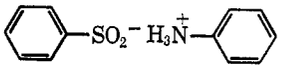


IV

Simple alkyl and aryl thiolsulfonates failed to undergo a detectable reaction with aromatic amines, but *o*-nitrophenyl benzenethiolsulfonate (V) reacted with aromatic amines in refluxing ethanol. Hence, *p*-anisidine, *p*-toluidine, and aniline gave the N-(*p*-methoxyphenyl)-*o*-nitrobenzenesulfenamide (VIa, 51%), N-(*p*-tolyl)-*o*-nitrobenzenesulfenamide (VIb, 89%), and N-phenyl-*o*-nitrobenzenesulfenamide (VIc), respectively. In the latter reaction the sulfenamide was isolated in very small yield, but the by-product, anilinium benzenesulfinate (VII), was isolated in 52%



V VIa, R = OCH_3; b, R = CH_3; c, R = H



VII

(1) (a) S. Smiles and D. T. Gibson, *J. Chem. Soc.*, 176 (1924); (b) D. T. Gibson and J. D. Loudon, *ibid.*, 487 (1937); (c) C. J. Miller and S. Smiles, *ibid.*, 224 (1925); (d) R. Otto and A. Rössig, *Ber.*, **20**, 2079 (1887); (e) R. Otto and E. Heydecke, *ibid.*, **25**, 1477 (1892); (f) L. D. Small, J. H. Bailey, and C. J. Cavallito, *J. Am. Chem. Soc.*, **71**, 3565 (1949); (g) H. Gilman, L. E. Smith, and H. H. Parker, *ibid.*, **47**, 851 (1925); (h) L. G. S. Brooker and S. Smiles, *J. Chem. Soc.*, 1723 (1926); (i) D. T. Gibson, *ibid.*, 2637 (1931); (j) H. J. Backer, *Rec. Trav. Chim.*, **71**, 409 (1952); (k) H. Kloosterziel and H. J. Backer, *ibid.*, 373; (l) D. W. Cowie and D. T. Gibson, *J. Chem. Soc.*, 306 (1933); (m) H. Lecher and A. Goebel, *Ber.*, **55**, 1483 (1922); (n) J. Michalski, J. Wieczorkowski, and T. Modro, *Roczniki Chem.*, **32**, 1409 (1958).

(2) (a) H. Lecher and K. Simon, *Ber.*, **54**, 632 (1921); (b) O. Foss, *Acta. Chem. Scand.*, **1**, 307 (1947); (c) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

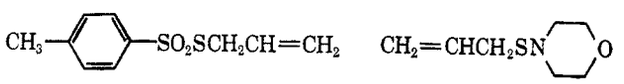
(3) B. G. Boldyrev and S. A. Kolesnikova, *Zh. Obshch. Khim.*, **35**, 198 (1965).

(4) J. E. Dunbar and J. H. Rogers, *Tetrahedron Letters*, 4291 (1965).

(5) L. Field, A. Ferretti, R. R. Crenshaw, and T. C. Owen, *J. Med. Chem.*, **7**, 39 (1964).

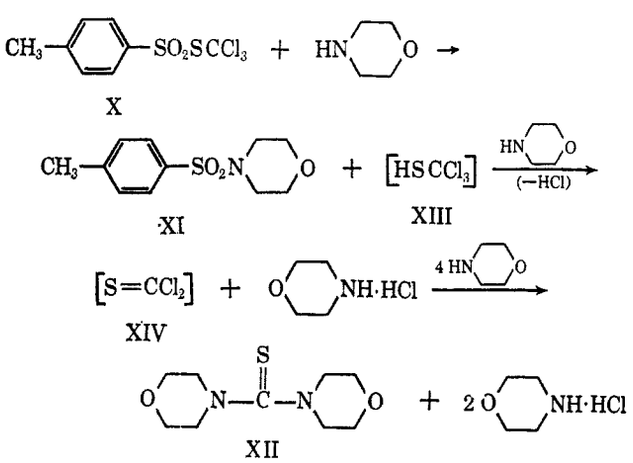
yield. Under the same conditions N-methylaniline failed to react with V. Since N-methylaniline is slightly more basic (pK_b 9.2) than aniline (pK_b 9.4), this failure to react may be attributed to the steric effect of the N-methyl group.

The usual procedure for the preparation of sulfenamides, involving the reaction of a sulfenyl chloride with an amine,[6] precludes the synthesis of allylsulfenamides, since the preparation of allylsulfenyl chloride would require chlorination of allyl mercaptan or disulfide with accompanying destruction of the double bond. Therefore, the reaction of allyl thiolsulfonates with amines provides a feasible synthesis of allylsulfenamides. The reaction of allyl *p*-toluenethiolsulfonate (VIII) and morpholine in ether at room temperature afforded 4-(allylthio)morpholine (IX) and morpholinium *p*-toluenesulfinate (III) in 85 and 100% yields, respectively.



VIII IX

Reactions of amines with trichloromethyl thiolsulfonates were found to proceed differently. When 1 mole of trichloromethyl *p*-toluenethiolsulfonate (X) was treated with 6 moles of morpholine in ether solution at room temperature, three products were obtained: *p*-toluenesulfonmorpholide (XI), morpholinium chloride, and 4,4′-(thiocarbonyl)dimorpholine (XII). The probable sequence of reactions would be the attack on the sulfonyl group by morpholine with the formation of XI and trichloromethylmercaptan (XIII). The intermediate XIII would then undergo immediate dehydrochlorination to give the second intermediate, thiophosgene (XIV), which would react with 4 moles more of morpholine to give XII.



X

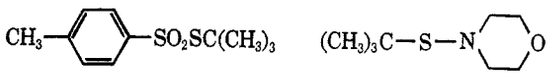
XI XIII

XIV

XII

Consideration was given to the possibility that steric hindrance of the trichloromethyl group was sufficient to divert the attack of the nucleophile to the sulfonyl group. If steric hindrance alone were responsible for this anomalous reaction, the same reaction should occur with *t*-butyl *p*-toluenethiolsulfonate (XV) and morpholine. However, when XV is treated with 2 moles of morpholine in refluxing ethanol, the reaction proceeds to the extent of 50% in 18 hr to give the "normal"

(6) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 1, Chemical Publishing Co., Inc., New York, N. Y., 1958, p 279.

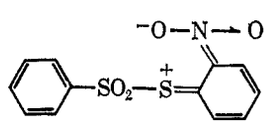


XV XVI

products, 4-(*t*-butylthio)morpholine (XVI) and morpholinium *p*-toluenesulfinate. None of the products which would have originated from the attack of morpholine on the sulfonyl group was detected. The equilibrium constant of the reaction is 6.1×10^{-3} compared to magnitudes in the order of 10^{-1} for those of the methyl thiolsulfonates (Table I).

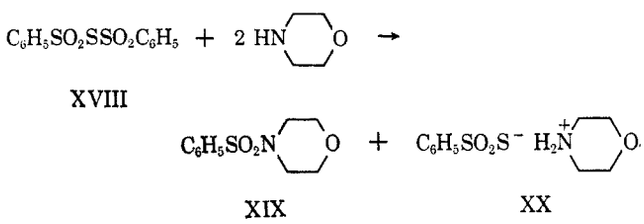
Since the *t*-butyl group offers more steric hindrance to the divalent sulfur atom in XV than does the trichloromethyl group in X, it is clear that the anomalous reaction of morpholine with the trichloromethyl thiolsulfonate is not caused by steric hindrance alone. In the case of the *t*-butyl thiolsulfonate only one electron-withdrawing group, the sulfonyl, is attached to the divalent sulfur; hence, the nonbonding electrons of the sulfur are displaced closer to the sulfonyl group, and nucleophilic attack on the sulfur is favored, the hindrance of the *t*-butyl group notwithstanding. The divalent sulfur of the trichloromethyl thiolsulfonate, however, is flanked by two opposing electronegative groups, with one essentially cancelling the ability of the other to displace the electron cloud from the sulfur. The electrophilicity of the divalent sulfur is therefore decreased, and an alternative attack upon the sulfonyl group by morpholine occurs.

The fact that *o*-nitrophenyl benzenethiolsulfonate reacts in the "normal" way with amines, giving sulfenamides and sulfinate salts as products, is resultant of unequal electron-withdrawing abilities of the sulfonyl and *o*-nitrophenyl groups. The stronger electronegative *o*-nitrophenyl group enhances the positive character of the sulfur atom, perhaps by the contribution of a resonance form such as XVII.



XVII

If the two flanking electronegative groups were identical, their electron-withdrawing abilities would be equally matched, and the electron cloud of the divalent sulfur should remain in place. Hence, a nucleophile would be expected to attack a sulfonyl group in preference to the divalent sulfur atom. Bis(benzenesulfonyl) sulfide (XVIII) reacted with morpholine at room temperature in ethyl ether to give benzenesulfonmorpholide (XIX) and morpholinium benzenethiosulfonate (XX). No 4-(benzenesulfonylthio)morpholine (XXI) or morpholinium benzenesulfinate (XXII) was obtained.

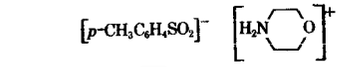
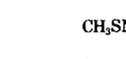
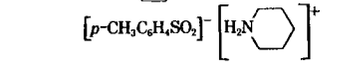
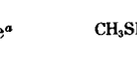
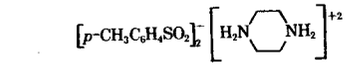
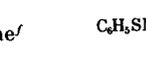
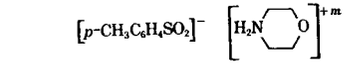
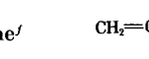
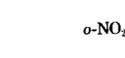
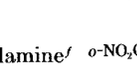
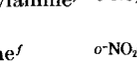
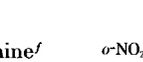
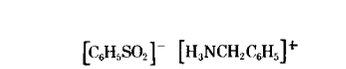


XVIII

XIX XX

TABLE II

SULFENAMIDES AND SULFINIC ACID SALTS FROM THIOLSULFONATES AND AMINES

Reactants		Products	Solvent (temp)	Time, hr	Yield, %	Mp or bp (mm), °C	Formula	Calcd, %			Found, %		
Thiolsulfonate	Amine	Sulfenamide and sulfinate salt						C	H	N	C	H	N
p-$CH_3C_6H_4SO_2SCH_3$	morpholine[a]		ether (ambient)	1	56	48–49 (5)[b]	$C_5H_{11}NOS$	45.1	8.33	10.5	45.0	8.22	10.4
					80	126–127.5[c]	$C_{11}H_{17}NO_3S$	54.3	7.04	5.76	54.4	7.22	5.44
p-$CH_3C_6H_4SO_2SCH_3$	piperidine[a]		methylene chloride (ambient)	1	55	43-44 (5)[d]	$C_6H_{13}NS$	54.9	9.98	10.7	55.3	10.2	10.9
					73	74-77[e]	$C_{12}H_{19}NO_2S$	59.7	7.93	5.81	59.6	8.20	5.85
p-$CH_3C_6H_4SO_2SCH_3$	diethylamine[f]	$CH_3SN(C_2H_5)_2$[g]	ether (ambient)	21	56	126–127 (760)[h] (lit. 127–128)	$C_5H_{13}NS$						
p-$CH_3C_6H_4SO_2SCH_3$	piperazine[a]		benzene (reflux)	2	71	140–142[i]	$C_6H_{14}N_2S_2$	40.4	7.91	15.7	40.6	7.84	15.8
					95	186–189[i]	$C_{18}H_{26}N_2O_4S_2$	54.2	6.58	7.03	54.4	6.77	7.21
$C_6H_5SO_2SC_6H_5$	morpholine[f]		ether (ambient)	2	90	33–36[j] (lit., 31–33)	$C_{10}H_{13}NOS$						
$C_6H_5SO_2SC_6H_5$	piperazine[a]		benzene (reflux)	2	68	164–166[i,k] (lit. 162–163)	$C_{16}H_{18}N_2S_2$						
p-$CH_3C_6H_4SO_2SCH_2C_6H_5$	morpholine[f]		ether (ambient)	19	76	74–76[l]	$C_{11}H_{15}NOS$	63.1	7.22	6.69	63.4	7.26	6.45
					100								
p-$CH_3C_6H_4SO_2SCH_2CH{=}CH_2$	morpholine[f]		ether (ambient)	17	85	40–41 (0.5)[n]	$C_7H_{13}NOS$	52.8	8.23	8.70	52.8	8.16	8.70
$CH_3SO_2S(CH_2)_4CH_3$	morpholine[f]		ether (ambient)	17	47	59–61 (0.3)[o]	$C_9H_{19}NOS$	57.1	10.1	7.40	57.4	10.1	7.57
$CH_3SO_2SCH_2CH_2SCH_3$	morpholine[p]		ether (ambient)	15	81	99 (1.2)	$C_7H_{15}NOS_2$	43.5	7.82	7.25	43.8	7.52	7.52
$C_6H_5SO_2SC_6H_4NO_2(o)$	ammonia[q]		methanol (ambient)	2	72	122–125.5[i,r] (lit. 124–125)	$C_6H_6N_2O_2S$						
$C_6H_5SO_2SC_6H_4NO_2(o)$	ethylenimine[p]		methylene chloride (ambient)	5	44	40.5–42[s]	$C_8H_8N_2O_2S$	49.0	4.11	14.3	49.0	4.15	14.0
$C_6H_5SO_2SC_6H_4NO_2(o)$	cyclohexylamine[f]		ether (ambient)	44	64	50–52[s,t] (lit. 51.5–52)	$C_{12}H_{16}N_2O_2S$						
$C_6H_5SO_2SC_6H_4NO_2(o)$	morpholine[f]		ether (ambient)	15	90	89–91[i,u] (lit. 89.5–90)	$C_{10}H_{12}N_2O_3S$						
$C_6H_5SO_2SC_6H_4NO_2(o)$	benzylamine[f]		ether (ambient)	15	79	59–61[i,u]	$C_{13}H_{12}N_2O_2S$						
					97	156–161[i,v] (lit. 153)	$C_{13}H_{15}NO_2S$						

$C_6H_5SO_2SC_6H_4NO_2(o)$	*p*-toluidine[f]	*o*-$NO_2C_6H_3SNHC_6H_4CH_3(p)$	ethanol (reflux)	1.5	89	136–138[i,w] (lit. 133)	$C_{13}H_{12}N_2O_2S$						
		$[C_6H_5SO_2^-][H_3NC_6H_4CH_3(p)]^+$			83	122–126[i,v] (lit. 123–125)	$C_{13}H_{15}NO_2S$						
$C_6H_5SO_2SC_6H_4NO_2(o)$	aniline[f]	*o*-$NO_2C_6H_3SNHC_6H_5$	ethanol (reflux)	33[x]	<10	94–97[w] (lit. 94)	$C_{12}H_{10}N_2O_2S$						
		$[C_6H_5SO_2^-][H_3NC_6H_5]^+$			52	130–132.5[v] (lit. 132)	$C_{12}H_{13}NO_2S$						
$C_6H_5SO_2SC_6H_4NO_2(o)$	*p*-anisidine[f]	*o*-$NO_2C_6H_3SNHC_6H_4OCH_3(p)$	ethanol (reflux)	1.5	51	138–140[t] (lit. 138–138.5)	$C_{13}H_{12}N_2O_3S$						
		$[C_6H_5SO_2^-][H_3NC_6H_4OCH_3(p)]^+$			100	127–129 (dec)[i]	$C_{13}H_{15}NO_3S$	58.8	5.70	5.28	58.7	5.62	5.06
p-$CH_3C_6H_4SO_2S$>$(CH_2)_5$ *p*-$CH_3C_6H_4SO_2S$	morpholine[w]	O>$NS(CH_2)_5SN$<O	ether (ambient)	18	83	33.5–36[z]	$C_{13}H_{26}N_2O_2S_2$	50.9	8.55	9.14	50.7	8.46	8.91
		$[p\text{-}CH_3C_6H_4SO_2^-][H_2N$>$O]^+$											

[a] Amine:thiolsulfonate molar ratio = 2:1. [b] $n^{25}D$ 1.4978. [c] Recrystallized from benzene. [d] $n^{25}D$ 1.4958. [e] Recrystallized from benzene–petroleum ether (bp 60–70°). [f] Amine:thiolsulfonate molar ratio = 4:1. [g] Sulfinate salt was not isolated. [h] $n^{25}D$ 1.4510, lit. $n^{25}D$ 1.453, H. J. Backer, *Rec. Trav. Chim.*, **70**, 254 (1951). [i] Recrystallized from isopropyl alcohol. [j] R. C. Kinstler (to American Cyanamid Co.), U. S. Patent 2,840,556 (June 24, 1958). [k] J. F. Smith (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,955,104 (Oct 4, 1960). [l] Recrystallized from petroleum ether (bp 60–70°), and then from methanol. [m] Characterized in experiment at beginning of table. [n] $n^{25}D$ 1.5086. [o] $n^{25}D$ 1.4825. [p] Amine:thiolsulfonate molar ratio = 3:1. [q] Concentrated ammonium hydroxide (300 ml) was used with 0.1 mole of thiosulfonate. [r] A. Baruffini and F. Gialdi, *Farmaco Ed., Sci.* **14**, 771 (1959); *Chem. Abstr.*, **54**, 8695 (1960). [s] Recrystallized from petroleum ether (bp 60–70°). [t] Recrystallized from ethanol. J. H. Billman and E. O'Mahoney, *J. Am. Chem. Soc.*, **61**, 2340 (1939). [u] N. Capron, R. Sasin, and G. S. Sasin, *J. Org. Chem.*, **21**, 362 (1956). [v] H. Bredereck and E. Bäder, *Chem. Ber.*, **87**, 129 (1954). [w] T. Zincke and F. Farr, *Ann.*, **391**, 57 (1912). [x] The sulfinate salt product was periodically removed during the reaction by evaporation of the ethanol and extraction of the residue with ether. The sulfinate salt was then removed by filtration, and the reaction was continued after replacement of the ether with ethanol. [y] Amine:thiolsulfonate molar ratio = 8:1. [z] Recrystallized from ether cooled in a Dry Ice–methylene chloride bath.

XXI

XXII

Experimental Section[7]

Equilibrium Constants of Amine–Thiolsulfonate Reactions.—Equilibrium constants of the amine–thiolsulfonate reactions (Table I) were determined at room temperature in an acetonitrile–water (7:1 by volume) solvent system by conductivity measurements of the concentrations of the morpholinium sulfinate salt products.

Thiolsulfonate Esters.—Methyl *p*-toluenethiolsulfonate,[11] phenyl benzenethiolsulfonate,[8] benzyl *p*-toluenethiolsulfonate,[9] allyl *p*-toluenethiolsulfonate,[10] *o*-nitrophenyl benzenethiolsulfonate,[9] and pentamethylene bis(*p*-toluenethiolsulfonate)[11] were synthesized according to the methods of the respective authors cited.

***n*-Pentyl Methanethiolsulfonate.**—To a suspension of 45.0 g (0.300 mole) of potassium methanethiosulfonate[12] in 450 ml of ethanol was added 45.3 g (0.300 mole) of *n*-pentyl bromide, and the mixture was heated under reflux with stirring for 16 hr. The reaction mixture was concentrated and cooled, and the potassium bromide by-product was removed by filtration. The ethanol was removed from the filtrate by evaporation *in vacuo* to give 48.4 g (89%) of yellow oil, $n^{25}D$ 1.4885. Fractionation gave the pure product as a colorless oil, bp 110–116° (0.9 mm), $n^{25}D$ 1.4928.

Anal. Calcd for $C_6H_{14}O_2S_2$: C, 39.53; H, 7.74; S, 35.17. Found: C, 39.59; H, 7.65; S, 35.63.

2-(Methylthio)ethyl Methanethiolsulfonate.—A mixture of 30.1 g (0.200 mole) of potassium methanethiosulfonate and 22.1 g (0.200 mole) of 2-chloroethyl methyl sulfide in 500 ml of ethanol was heated under reflux with stirring for 6 hr and then allowed to cool to room temperature. The potassium chloride was removed by filtration and the ethanol was removed from the filtrate by evaporation *in vacuo*, leaving a colorless oil. After filtration to remove a small amount of solid impurity, the oil was dissolved in ether at room temperature, and the solution was cooled in a Dry Ice–methylene chloride bath. The product crystallized as 33.3 g (90%) of white crystals, mp 4–5°, $n^{25}D$ 1.5566.

Anal. Calcd for $C_4H_{10}O_2S_3$: C, 25.79; H, 5.41; S, 51.63. Found: C, 25.92; H, 5.26; S, 51.70.

Reaction of Amines with Thiolsulfonates. General Procedure.—Two equivalents (or an excess) of the primary or secondary amine were added in one portion with stirring to a solution of one equivalent of the thiolsulfonate in 1 to 3 l. of the appropriate solvent. The reaction was allowed to remain at room temperature or at the reflux temperature of the solvent for a period of time ranging from one to 44 hr. The water-soluble sulfinic acid salt product was either collected by filtration or removed by contacting the reaction mixture with water and discarding the aqueous portion. In the cases in which water-immiscible reaction solvents were used, the solution was washed with water and dried over anhydrous magnesium sulfate. The solvent was then removed by evaporation *in vacuo*, and the remaining crude sulfenamide was purified either by distillation or by crystallization. In cases where a water-miscible solvent was used as a reaction medium, the reaction mixture was poured into water and the crude product either extracted with an appropriate solvent and treated as above or collected on a filter, dried, and recrystallized.

Reaction of Morpholinium *p*-Toluenesulfinate (III) and 4-(Methylthio)morpholine(II).—A mixture of 6.75 g (0.0278 mole) of morpholinium *p*-toluenesulfinate and 3.70 g (0.0278 mole) of 4-(methylthio)morpholine in 150 ml of ether was left at room temperature for 20 hr. The remaining morpholinium salt was filtered off, and the ether filtrate was washed several times with water. The ethereal layer was dried over anhydrous magnesium sulfate, then evaporated to dryness, leaving a colorless oil. A gas–liquid partition chromatogram indicated the presence of ap-

(7) All melting points are uncorrected.

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proximately equal amounts of 4-(methylthio)morpholine and methyl *p*-toluenethiolsulfonate. An infrared spectrum of the oil showed characteristic absorption bands of the thiolsulfonate group (1140 and 1325 cm^{-1}) and the symmetrical (700 cm^{-1}) and unsymmetrical (950 cm^{-1}) stretching bands of the C–S–N sulfenamide linkage. The oil was triturated in methylcyclohexane and the white insoluble solid collected on a filter. This substance proved to be methyl *p*-toluenethiolsulfonate, mp 56–59° (1.68 g, 30%).

Reaction of Morpholine with Trichloromethyl *p*-Toluenethiolsulfonate (X).—Morpholine (52.2 g, 0.600 mole) was added dropwise to a stirred solution of 30.6 g (0.100 mole) of trichloromethyl *p*-toluenethiolsulfonate[13] in 400 ml of ether at 5°. A precipitate commenced to form immediately after the beginning of the addition. After the addition was complete the mixture was stirred at 5° for 30 min, then for an additional 20 min at room temperature. The precipitate was collected on a filter and washed with acetone to give 26.8 g (72%) of a white, water-soluble solid, mp 175–178°. The infrared spectrum of this substance was identical with that of an authentic sample of morpholinium chloride.

The solvent was evaporated from the combined acetone washings and ether filtrate. The semisolid residue was extracted with hot water (extract A), and the solid (19.7 g, 82%, mp 138–147°) was collected on a filter and recrystallized from ethanol to give colorless needles, mp 147.5–148.5° (*p*-toluenesulfonmorpholide lit.[14] mp 147°). The infrared spectrum of this substance and that of an authentic sample of the sulfonamide were identical.

Anal. Calcd for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.81. Found: C, 55.05; H, 6.32; N, 5.69.

Extract A was concentrated and cooled three successive times to give 12.7 g (59%) of colorless crystals, mp 86–88.5°. Recrystallization from water gave the pure substance, mp 88–89°, which proved to be 4,4′-(thiocarbonyl)dimorpholine (lit.[15] mp 89.5–90°). The infrared spectrum of the substance and that of an authentic sample were identical.

Anal. Calcd for $C_9H_{16}N_2O_2S$: C, 50.0; H, 7.46; N, 13.0. Found: C, 50.1; H, 7.41; N, 12.9.

Reaction of Morpholine with *t*-Butyl *p*-Toluenethiolsulfonate (XV).—Morpholine (17.4 g, 0.200 mole) was added to a warm solution of 24.4 g (0.100 mole) of *t*-butyl *p*-toluenethiolsulfonate[16] in 100 ml of methanol, and the reaction mixture was heated under reflux. After 3.5 hr, vpc analysis indicated a 48% conversion of the thiolsulfonate, and after a total of 18.5 hr of heating a 58% conversion was indicated by vpc. The heating was then stopped, and the methanol was removed by evaporation *in vacuo*, leaving a residue consisting of an oil and a solid. The residue was extracted at room temperature with carbon tetrachloride, and the insoluble solid was collected on a filter. This solid was extracted at room temperature with acetone, leaving 12.1 g (50%) of white solid, mp 126–127.5°. The infrared spectrum was identical with that of an authentic sample of morpholinium *p*-toluenesulfinate. (The acetone wash, upon evaporation, yielded only a trace of residue.)

The carbon tetrachloride extract was washed with three portions of water and dried over anhydrous magnesium sulfate. The solvent was then removed by evaporation *in vacuo*, leaving 12.4 g of yellow oil which, upon standing at room temperature for several hours, yielded 4.4 g of white crystalline solid, melting range 60–69°. Vpc analysis proved this substance to be unreacted *t*-butyl *p*-toluenethiolsulfonate. The remaining liquid was purified by distillation, giving a colorless oil, bp 57° (1.8 mm), $n^{25}D$ 1.4748, which proved to be 4-(*t*-butylthio)morpholine [lit.[17] bp 50° (1.0 mm), $n^{25}D$ 1.4745].

Anal. Calcd for $C_8H_{17}NOS$: C, 54.8; H, 9.78; N, 7.99. Found: C, 54.9; H, 9.53; N, 7.86.

The nmr spectrum (using tetramethylsilane as an internal standard) showed a single band absorption at −1.25 ppm of the nine equivalent *t*-butyl protons, a grouping from −2.87 to −3.08 ppm representing the four protons on the carbons adjacent to nitrogen, and a group from −3.58 to −3.79 ppm representing the four protons on the carbons adjacent to oxygen.

Reaction of Morpholine with Bis(benzenesulfonyl) Sulfide (XVIII).—Morpholine (5.5 g, 0.064 mole) was added to a stirred slurry of 10.0 g (0.0318 mole) of bis(benzenesulfonyl) sulfide[18] in 200 ml of ethyl ether, and the reaction mixture was allowed to stand at room temperature for 18 hr. The white precipitate was then collected on a filter and washed with water. The water-insoluble substance was recrystallized from 2-propanol to give 5.6 g (78%) of colorless crystals, mp 118–120°, which proved to be benzenesulfonmorpholide (lit.[19] mp 118–120°). The water was removed from the aqueous solution by evaporation *in vacuo*, leaving 5.9 g of white solid which, after recrystallization from 2-propanol, gave the pure morpholinium benzenethiosulfonate, mp 142–144°.

Anal. Calcd for $C_{10}H_{15}NO_3S_2$: C, 46.0; H, 5.79; N, 5.36. Found: C, 46.1; H, 5.83; N, 5.27.

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