purging unreacted $COCl_2$ and HCl, the reaction mixture was cooled in Dry Ice–acetone, and the precipitate formed was filtered, washed with a small portion of CCl_4, and dried *in vacuo* to give 2.6 g (51%, based on $COCl_2$) of **19**, which was recrystallized twice from acetone to give pale yellow plates: mp 151–153°; nmr ($CDCl_3$) τ 2.44 (s, 1 H), 2.72 (s, 1 H), 7.22 (s, 3 H), 7.52 (s, 3 H), and 7.61 (s, 3 H).

Anal. Calcd for $C_{12}H_{11}NCl_2$: C, 60.02; H, 4.62; N, 5.83. Found: C, 59.88; H, 4.57; N, 5.68.

Reaction of 2d with CH_3CN and HCl.—In a 20-ml sealed glass tube, 0.8 g of the mixture of **2d** and **1d** (the content of **2d** is *ca.* 0.31 g), CH_3CN (3 g), and HCl (0.5 g) were heated at 100–105° for 5 days. The precipitate formed was filtered, washed with CH_3CN, dried *in vacuo*, and sublimed under reduced pressure to give 7 mg of **17**. The filtrate was concentrated and chromatographed over alumina. Petroleum ether eluted 25 mg of **21** (8%): mp 111–117°; mass spectrum (70 eV) *m/e* (rel intensity) 227 (66, $M^+ + 2$), 225 (100, M^+), 210 (43), 190 (36), 154 (32), and 127 (26).

Reaction of 2e with CH_3CN and HCl at 100–105°.—In a 20-ml sealed glass tube 0.5 g of the mixture of **2e** and **1e** (the content of **2e** is *ca.* 0.28 g), CH_3CN (4 g), and HCl (0.4 g) were heated at 100–105° for 140 hr. From the reaction mixture 6 mg of brown powder was isolated by filtration. It was sublimed under reduced pressure to give the yellow powder of 3-chloro-7-nitroisocarbostyril: mp above 300°; ir (KBr) 1675 cm^{-1} (C═O); mass spectrum (70 eV) *m/e* (rel intensity) 226 (29, $M^+ + 2$), 224 (85, M^+), 194 (93), 178 (40), 150 (51), 130 (100), 123 (49), and 114 (65).

Reaction of 2e with CH_3CN and HCl at 55–60°.—In a 20-ml sealed glass tube 0.67 g of the mixture of **2e** and **1e** (the content of **2e** is *ca.* 0.37 g), CH_3CN (4 g), and HCl (0.5 g) were heated at 55–60° for 7 days. The precipitate formed was filtered, washed with CH_3CN, and dried *in vacuo* to give brown powder of 6-chloro-2-(*p*-nitrobenzyl)-4(3*H*)-pyrimidone (81 mg, 22%), which was recrystallized from CH_3CN to give yellow plates: mp 250–259° dec; ir (KBr) 1675 cm^{-1} (C═O); nmr (CF_3COOH) τ doublets centered at 1.65 (2 H) and 2.35 (2 H, A_2B_2 system), 3.10 (s, 1 H), and 5.47 (s, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 267 (26, $M^+ + 2$), 265 (70, M^+), 264 (100), 116 (68), 106 (50), 89 (92), 68 (78), and 63 (50).

Anal. Calcd for $C_{11}H_8N_3O_3Cl$: C, 49.73; H, 3.04; N, 15.82. Found: C, 49.79; H, 2.77; N, 16.01.

Registry No.—**2a**, 31579-10-9; **2c**, 31579-11-0; **2d**, 31579-12-1; **2e**, 31579-13-2; **3a**, 31579-14-3; **3b**, 31579-15-4; **3c**, 31579-16-5; **3d**, 31579-17-6; **3e**, 31579-18-7; **3f**, 31579-19-8; **6a**, 31579-20-1; **6b**, 31579-21-2; **6c**, 31579-22-3; **6d**, 31579-23-4; **6e**, 31579-24-5; **6f**, 31579-25-6; **13**, 31579-26-7; **14**, 31579-27-8; **15**, 31579-28-9; **16**, 31579-29-0; **18**, 31579-30-3; **19**, 31579-31-4; **21**, 31579-32-5; isocarbostyryl, 31579-33-6; 3-chloro-7-nitroisocarbostyryl, 24633-93-0; 6-chloro-2-(*p*-nitrobenzyl)-4(3*H*)-pyrimidone, 31579-35-8.

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A Novel Reaction of Acetylsulfenyl Chloride with Activated Aromatic Compounds

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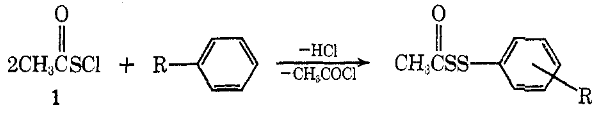
A novel aromatic sulfuration reaction is described. The reaction of acetylsulfenyl chloride with activated aromatic compounds such as anisole, *m*-xylene, toluene, and phenol yields acetyl aryl disulfides. A mechanism involving a tetravalent sulfur intermediate is proposed.

Preceding papers on aromatic sulfurations have shown that a catalytic amount of iron powder promotes the reaction of aromatics with the compounds containing bivalent sulfur-chlorine bonds. The reactions with sulfur chlorides[1] and sulfenyl chlorides[2] yield symmetric sulfides and asymmetric sulfides, respectively. On the other hand, benzenethiosulfenyl chlorides give disulfide or monosulfide depending on whether or not they have an ortho group.[3]

With a view to extending the scope of the aromatic sulfuration reaction, our attention was attracted to acetylsulfenyl chloride (**1**) which also has a sulfur-chlorine bond. **1** was first synthesized by Böhme and Clement,[4] and since then there have been several reports on the chemical behavior of **1**. However, previous works have dealt almost entirely with the reaction between **1** and such functional groups as active hydrogen[4–6] and olefinic double bonds.[7,8] The only example involving the reaction of **1** with aromatic compounds is the one with phenols[9] (*vide infra*).

In the present paper a novel reaction of **1** with activated aromatic compounds is described, which results in the formation of acetyl aryl disulfide (**2**). To



1

2a, R = 4-CH_3O
b, R = 2,4-di-CH_3
c, R = 2-CH_3
d, R = 4-CH_3
e, R = 4-HO

our knowledge this is the first example of asymmetric disulfide formation in aromatic sulfuration with sulfenyl halides.

A methylene chloride solution of a 1:1 mixture of acetylsulfenyl chloride (**1**) and anisole was stirred for 40 hr at room temperature and then refluxed for 2 hr. The main product was acetyl *p*-anisyl disulfide (**2a**) instead of acetyl *p*-anisyl sulfide, the product expected on the basis of analogy with previous studies. Confirmation of structure **2a** was obtained from ele-

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[1] T. Fujisawa, N. Ohtsuka, T. Kobori, and G. Tsuchihashi, *Tetrahedron Lett.*, 4533 (1968).

[2] T. Fujisawa, T. Kobori, N. Ohtsuka, and G. Tsuchihashi, *ibid.*, 5071 (1968).

[3] T. Fujisawa, T. Kobori, and G. Tsuchihashi, *ibid.*, 4291 (1969).

[4] H. Böhme and M. Clement, *Justus Liebigs Ann. Chem.*, **576**, 61 (1952).

[5] H. Böhme and G. Zinner, *ibid.*, **585**, 142 (1954).

[6] H. Böhme, F. Freimuth, and E. Mundlos, *Chem. Ber.*, **87**, 1661 (1954).

[7] H. Böhme, H. Bezzenberger, and H. D. Stachel, *Justus Liebigs Ann. Chem.*, **602**, 1 (1957).

[8] S. Z. Ivin and V. K. Promonenkov, *Otd. Obshch. Tekh. Khim.*, 139 (1967); *Chem. Abstr.*, **68**, 114701p (1968).

[9] H. Böhme and H. W. Goubeaud, *Chem. Ber.*, **92**, 366 (1959).

mental analysis and ir, nmr, and mass spectra in addition to independent synthesis from **1** and *p*-methoxythiophenol. Di-*p*-anisyl sulfide and di-*p*-anisyl disulfide were obtained simultaneously as by-products. When acetonitrile was employed as the reaction medium, a somewhat higher yield of **2a** resulted.

Compared to aromatic sulfurations with sulfur chlorides[1] and common sulfenyl chlorides,[2] this reaction was less affected by catalysts. As shown in Table I, aluminum chloride and concentrated sulfuric acid did not catalyze the reaction. Iron powder and ferric chloride, which are known to be effective catalysts in aromatic sulfuration, only promoted the side reactions, *i.e.*, the formation of *p*-methoxyacetophenone[10] and acetyl *p*-anisyl sulfide.

TABLE I

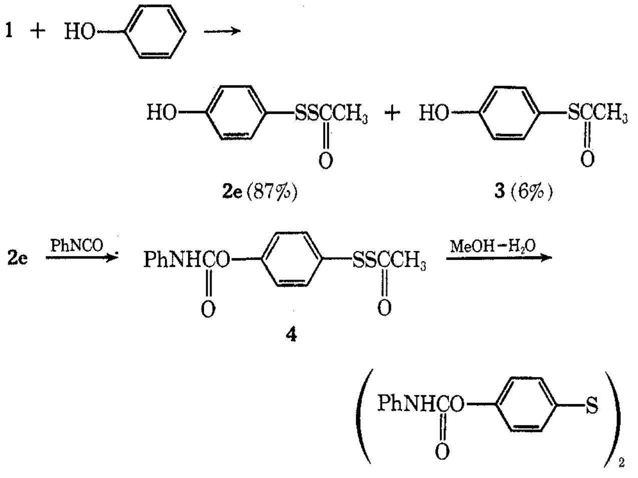
REACTION OF ACETYLSULFENYL CHLORIDE (1) WITH ANISOLE[a]

Catalyst	Medium	Product[b] yield, %[c]				
		AcAn	AcSAn	AcSSAn	AnSAn	AnSSAn
	CH_2Cl_2	0	0	61	2	9
	CH_3CN	0	0	75	2	13
$AlCl_3$	CH_2Cl_2	0	0	74	3	2
H_2SO_4	CH_2Cl_2	0	0	70	4	8
Fe	CH_2Cl_2	6	6	66	3	15
$FeCl_3$	CH_2Cl_2	7	4	45	2	25

[a] Reaction conditions: 1:anisole = 1:1; 25° (40 hr), reflux (2 hr). [b] Ac = CH_3CO–, An = *p*-$CH_3OC_6H_4$–. [c] Based on 1.

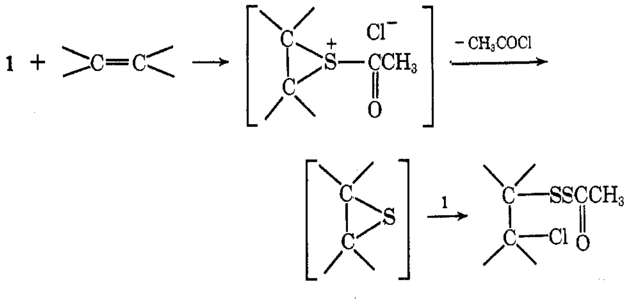
Other activated aromatic compounds also underwent a similar reaction. When a *m*-xylene solution of **1** was gradually heated up to 125° in 12 hr, acetyl 2,4-xylyl disulfide (**2b**) was obtained in 49% yield. Acetyl tolyl disulfide was obtained as a mixture of the ortho isomer **2c** and the para isomer **2d** in 26% combined yield by heating a toluene solution of **1** in the presence of iron powder. Benzene did not give any identifiable product under more drastic conditions. The properties of **2** thus obtained are summarized in Table II. The ir spectrum of **2** contains two characteristic bands in the region 1735–1700 cm^{-1}, assignable to a carbonyl group. In addition, two other absorption frequencies are observed, one at ~1105 cm^{-1} and the other at ~935 cm^{-1}. These bands would generally be assigned to a –C–C(O)– stretch and a –C(O)–S– stretch, respectively from analogy with the case of thiol esters.[11] The nmr chemical shifts of the protons ortho to the sulfur atom of **2** are observed at lower field than those of the corresponding acetyl aryl sulfide. A similar effect of the polysulfide linkage has already been observed for aryl polysulfides.[12]

The literature contains only one reference to the reaction of **1** with aromatic compounds (*vide supra*). It has been reported that the reaction product of **1** and phenol was acetyl 4-hydroxyphenyl sulfide (**3**).[9] In view of our results mentioned above, however, it would be reasonable to expect the formation of acetyl 4-hydroxyphenyl disulfide (**2e**) in the reaction of **1** with phenol. Accordingly, we reinvestigated the reaction. As will now be seen, this prediction is amply fulfilled. An ether solution of **1** and excess phenol was stirred at room temperature for 40 hr, then refluxed for 5 hr. An oily material was obtained by removal of the solvent and excess phenol. The nmr spectrum of the oil contains two AB quartets. Signals consistent with **2e** [δ 6.71 (d, J = 9.0 Hz), 7.39 (d, J = 9.0 Hz)] indicate its presence in this crude product, and the other AB quartet [δ 6.71 (d, J = 9.0 Hz), 7.15 (d, J = 9.0 Hz)] is consistent with structure **3**. In addition, the mass spectrum of the oil supports the presence of **2e** (*m/e* 200) and **3** (*m/e* 168). The yields of **2e** and **3** were estimated as 87 and 6%, respectively, from the nmr integral ratio. Subsequent treatment of the crude product with phenyl isocyanate in the presence of a catalytic amount of aluminum chloride gave the urethane derivative of **2e**, 4-acetyldithiophenyl phenylcarbamate (**4**). The physical properties of **4** are also listed in Table II. **4** was rather unstable and decomposed to a symmetric disulfide (**5**) when boiled in methanol–water. Consequently, it is concluded that aromatic sulfuration by **1** leads predominantly to the formation of acetyl aryl disulfides.



2e (87%) **3** (6%) **4** **5**

Concerning the reaction of **1**, another case of disulfide formation has been found in the reaction with olefins.[7,8,13] Böhme and coworkers proposed a mechanism in which ethylene sulfide was suggested as a possible intermediate.[7] It seems that both reactions, aromatic substitution by **1** and addition of **1** to olefins, ought to proceed by a similar mechanism, since they are electrophilic reactions. In the former case, how-



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[10] Control experiments proved that the formation of *p*-methoxyacetophenone can be ascribed to the reaction of anisole with acetyl chloride, which may be formed during the reaction of 1 with anisole, in the presence of iron powder or ferric chloride.

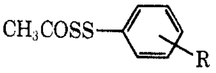
[11] R. A. Nyquist and W. J. Potes, *Spectrochim. Acta*, **7**, 514 (1959).

[12] T. Fujisawa and G. Tsuchihashi, *Bull. Chem. Soc. Jap.*, **43**, 3615 (1970).

[13] Chlorocarbonylsulfenyl chloride also adds to olefins in a molar ratio of 2:1 to form 2-chloroalkyl chlorocarbonyl disulfides with elimination of phosgene: G. Zumach and E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **9**, 54 (1970).

TABLE II

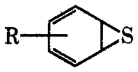
PROPERTIES OF ACETYL ARYL DISULFIDES (2)



	R	Bp, °C (mm)	ν_{max}, cm^{-1} C=O	-C-C<	>C-S-	Nmr (in CCl_4, δ)
2a	4-Methoxy	132 (1.5)	1730 1705[a]	1105	935	2.32 (s, 3 H), 3.70 (s, 3 H), 6.69 (d, J = 9 Hz, 2 H), 7.41 (d, J = 9 Hz, 2 H)
2b	2,4-Dimethyl	146–147 (7)	1735 1705[a]	1105	938	2.22 (s, 3 H), 2.28 (s, 3 H), 2.42 (s, 3 H) 6.81 (d, J = 8 Hz, 1 H), 6.86 (s, 1 H), 7.37 (d, J = 8 Hz, 1 H)
2c	2-Methyl	109–110 (1)	1730 1705[a]	1105	935	2.31 (s, 3 H), 2.46 (s, 3 H), 6.95–7.05 (m, 3 H), 7.40–7.50 (m, 1 H)
2d	4-Methyl	114–116 (1)	1730 1705[a]	1105	935	2.27 (s, 3 H), 2.32 (s, 3 H), 6.97 (d, J = 8.5 Hz, 2 H), 7.31 (d, J = 8.5 Hz, 2 H)
4	4-Phenylcarbamoyloxy	(109–112)[b]	1735 1715	1108	935	2.44 (s, 3 H), 7.06–7.75 (m, 5 H), 7.10 (d, J = 9.4 Hz, 2 H), 7.53 (d, J = 9.4 Hz, 2 H)[c]

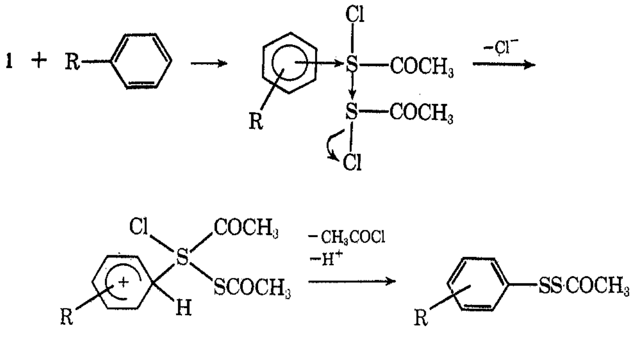
[a] Shoulder. [b] Mp, °C. [c] In $CDCl_3$.

ever, the formation of an episulfide such as 6 would be energetically unfavorable.



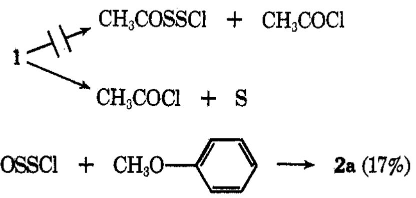
6

The following three pathways (A–C) are conceivable for the formation of 2. (A) 1 disproportionates to acetylthiosulfenyl chloride and acetyl chloride. The former reacts with aromatics to give 2. (B) Acetyl aryl sulfide is formed at first and then it reacts rapidly with another molecule of 1 to give 2. A similar reaction has been reported by Douglass:[14] methanesulfenyl chloride reacts readily with methyl thiolacetate, forming methyl disulfide and acetyl chloride. (C) Elimination of acetyl chloride from an intermediate containing tetravalent sulfur[15] results in the formation of 2.

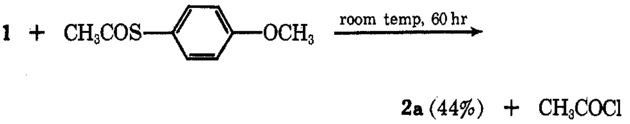


2

A control experiment proved that 1 does not disproportionate but degrades to acetyl chloride with the elimination of elemental sulfur. A second control experiment revealed that acetylthiosulfenyl chloride is less reactive than 1 toward anisole, and the yield of 2a is only 17% under conditions similar to those employed for the uncatalyzed reaction of 1 with anisole. Thus path A seems unlikely.



When acetyl anisyl sulfide was allowed to react with 1 in methylene chloride at room temperature for 60 hr, the yield of 2a was 44%.



Subsequent refluxing for 2 hr caused an increase of the yield to 47% and 1 still remained in the reaction mixture. If the reaction in path B were operative, the reaction should be very fast and quantitative, because acetyl anisyl sulfide was not found in the reaction products of 1 and anisole in the absence of catalysts. Since this is not what was observed, selective formation of 2a in the present study cannot be completely accounted for by path B. Then we prefer path C, although the evidence is not conclusive. Following this mechanism, the formation of disulfide in the reaction of 1 with olefins can also be understood by simply replacing the aromatic structure in path C by a carbon–carbon double bond.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were run on a Perkin-Elmer 337 spectrophotometer. All nmr spectra were recorded on a Varian HA-100 spectrometer. Chemical shifts of nmr spectra are reported in parts per million downfield from internal TMS (δ). Mass spectra were obtained on a Hitachi mass spectrometer for all compounds. Fragments are reported as *m/e*. Glpc analyses were conducted using a Hitachi K 53 chromatograph with a 3% SE-30 column at 180°. For analytical determinations correction factors for weight ratio/area ratio data were determined with standards containing the same compounds. Acetylsulfenyl chloride (1) was prepared by treating diacetyl sulfide with sulfuryl chloride according to the method of Böhme and Clement.[4] Acetylthiosulfenyl chloride was prepared by treating thiolacetic acid with chlorine.[4]

Reaction of 1 with Anisole. A. In Methylene Chloride.—

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[14] I. B. Douglass, *J. Org. Chem.*, **24**, 2004 (1959).

[15] For recent discussions of tetravalent sulfur intermediates see B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969); D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); C. R. Johnson and J. J. Rigau, *ibid.*, **91**, 5389 (1969); R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969).

To a solution of anisole (4.0 g, 37 mmol) in methylene chloride (20 ml) cooled to −20° was added slowly a solution of acetylsulfenyl chloride (**1**) (4.0 g, 36 mmol) in methylene chloride (20 ml). The mixture was stirred for 40 hr at room temperature and then heated under reflux for 2 hr. Distillation of the solvent and unreacted anisole under reduced pressure gave 3.3 g of a yellow liquid. The products were determined and identified by glpc. The retention times were identical with those of authentic samples. The compounds identified were acetyl *p*-anisyl disulfide (**2a**) (61%), di-*p*-anisyl sulfide (2%), and di-*p*-anisyl disulfide (9%). Distillation of the reaction mixture gave 1.6 g of pure **2a**, bp 132–134° (2 mm); ir, nmr, and mass spectra are identical with those of an authentic sample (*vide infra*).

Anal. Calcd for $C_9H_{10}O_2S_2$: C, 50.44; H, 4.70; S, 29.92. Found: C, 49.86; H, 4.83; S, 29.94.

B. In Acetonitrile.—The reaction between **1** (4.5 g, 41 mmol) and anisole (4.4 g, 41 mmol) in acetonitrile (40 ml) was carried out essentially as in methylene chloride. The products were analyzed by glpc (Table I).

C. In Methylene Chloride in the Presence of Aluminum Chloride.—The reaction between **1** (5.0 g, 45 mmol) and anisole (5.0 g, 46 mmol) in the presence of aluminum chloride (*ca.* 50 mg) was carried out essentially as in the absence of the catalyst. The identified products were listed in Table I.

D. In Methylene Chloride in the Presence of Concentrated Sulfuric Acid.—To a solution of anisole (5.0 g, 46 mmol) and concentrated sulfuric acid (*ca.* 50 mg) in methylene chloride (20 ml) cooled to −20° was added dropwise a solution of **1** (5.0 g, 45 mmol) in methylene chloride (20 ml). The mixture was stirred for 40 hr at room temperature and then heated under reflux for 2 hr. After removal of the solvent and unreacted anisole under reduced pressure, the residual liquid was dissolved in benzene, washed several times with water, and dried; the benzene was removed. The products were analyzed by glpc (Table I).

E. In Methylene Chloride in the Presence of Iron Powder.—A solution of **1** (5.0 g, 45 mmol) in methylene chloride (20 ml) was added slowly to a cooled (−20°) mixture of anisole (5.0 g, 46 mmol), iron powder (*ca.* 50 mg), and methylene chloride (20 ml). The system was stirred for 40 hr at room temperature and then heated under reflux for 2 hr. After work-up the products were analyzed by glpc. The compounds identified were *p*-methoxyacetophenone (6%), acetyl *p*-anisyl sulfide (6%), **2a** (66%), di-*p*-anisyl sulfide (3%), and di-*p*-anisyl disulfide (15%).

F. In Methylene Chloride in the Presence of Ferric Chloride.—The reaction between **1** (5.0 g, 45 mmol) and anisole (5.0 g, 46 mmol) in the presence of ferric chloride (*ca.* 50 mg) was carried out essentially as in the presence of iron powder. The products were analyzed by glpc (Table I).

Reaction of 1 with *m*-Xylene.—A solution of **1** (4.2 g, 38 mmol) in *m*-xylene (26.0 g, 245 mmol) was stirred for 10 hr at room temperature and then heated gradually up to 125° in 12 hr. The solvent was removed under reduced pressure to give 2.8 g of a dark brown liquid. Glpc indicated the presence of 2,4-dimethylacetophenone (2%), acetyl 2,4-xylyl sulfide (2%), acetyl 2,4-xylyl disulfide (**2b**) (49%), and bis(2,4-xylyl) sulfide (7%). The ir and nmr spectra of **2b** isolated by preparative glpc were identical with those of an authentic sample (*vide infra*).

Reaction of 1 with Toluene.—Iron powder (*ca.* 50 mg) was added to a solution of **1** (9.2 g, 83 mmol) in toluene (40.0 g, 430 mmol). The mixture was stirred for 7 hr at room temperature and then heated to 85° in 18 hr. Distillation of the solvent under reduced pressure and filtration of solid materials gave 2.7 g of a black liquid. Glpc indicated the presence of *o*- and *p*-methylacetophenone (1%), acetyl tolyl sulfide (3%), and the acetyl tolyl disulfides **2c** and **2d** (26% combined).

Reaction of 1 with Phenol.—A solution of **1** (4.2 g, 38 mmol) in ether (20 ml) was added dropwise to a solution of phenol (11.0 g, 117 mmol) in ether (20 ml). The mixture was stirred for 40 hr at room temperature and then heated under reflux for 5 hr. A pale yellow oil (3.7 g) was obtained by removal of ether and excess phenol under reduced pressure: ir (neat) 3400 (ν_{OH}), 1760 (shoulder), 1740, 1700 ($\nu_{C=O}$), 1110 ($\nu_{CC(O)}$), and 940 cm^{-1} ($\nu_{C(O)S}$); nmr ($CDCl_3$) δ 2.40 (s), 6.06 (s), 6.35 (s), 6.71 (d, J = 9 Hz), 7.15 (d, J = 9 Hz), and 7.39 (d, J = 9 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 200 M$^+$ (8), 168 (1), 158 (18), 136 (13), 128 (9), 125 (14), 95 (8), 94 (100), 65 (17), 43 (91).

4-Acetyldithiophenyl Phenylcarbamate (4).—A mixture of the adduct from above (3.4 g, 17 mmol as **2e**), phenyl isocyanate (2.1 g, 17 mmol), a catalytic amount of aluminum chloride, and ether (30 ml) was stirred for 2 hr at room temperature and then heated under reflux for 15 hr. The reaction mixture was filtered and concentrated, and the resulting white solid was triturated with *n*-hexane to give 3.9 g of **4** (72%). Recrystallization from *n*-hexane gave **4** in pure form: mp 109–112°; mass spectrum (70 eV) *m/e* 319 M$^+$ (<1), 119 (100); ir and nmr data are listed in Table II.

Anal. Calcd for $C_{15}H_{13}NO_3S_2$: C, 56.41; H, 4.10; N, 4.38; S, 20.08. Found: C, 56.61; H, 4.31; N, 4.49; S, 19.87.

Attempts to recrystallize **4** from methanol-water resulted in the formation of bis(4-phenylcarbamoyloxyphenyl) disulfide (**5**): mp 190–191°; ir (KBr) 3275 (ν_{NH}), 1715 ($\nu_{C=O}$); nmr (DMSO-d_6) δ 7.00–7.82 (m).

Anal. Calcd for $C_{26}H_{20}N_2O_4S_2$: C, 63.91; H, 4.12; N, 5.73; S, 13.12. Found: C, 63.90; H, 4.16; N, 5.64; S, 13.15.

Independent Synthesis of 2.—Authentic acetyl aryl disulfides were synthesized by the reaction of **1** with the corresponding thiols. Ir and nmr data are summarized in Table II.

Acetyl *p*-Anisyl Disulfide (2a).—To a solution of *p*-methoxythiophenol (3.2 g, 23 mmol) in ether (25 ml) cooled to −20° was added dropwise a solution of **1** (2.5 g, 23 mmol) in ether (15 ml). After stirring for 6 hr at room temperature, the reaction mixture was heated under reflux for 1 hr. Removal of ether yielded **2a** (4.0 g, 83%) after distillation, bp 132° (1.5 mm), mass spectrum (70 eV) *m/e* 214 M$^+$.

Anal. Calcd for $C_9H_{10}O_2S_2$: C, 50.44; H, 4.70; S, 29.92. Found: C, 50.49; H, 4.70; S, 29.94.

Acetyl 2,4-Xylyl Disulfide (2b).—The reaction of **1** (2.5 g, 23 mmol) with 2,4-thioxylenol (2.5 g, 18 mmol) in ether (40 ml) afforded 2.3 g of **2b** (60%) after distillation, bp 146–147° (7 mm), mass spectrum (70 eV) *m/e* 212 M$^+$.

Anal. Calcd for $C_{10}H_{12}OS_2$: C, 56.57; H, 5.70; S, 30.20. Found: C, 56.42; H, 5.69; S, 30.08.

Acetyl *o*-Tolyl Disulfide (2c).—A solution of *o*-thiocresol (4.5 g, 36 mmol) in ether (20 ml) was treated with a solution of **1** (4.0 g, 36 mmol) in ether (20 ml) at −20°. Distillation gave 6.0 g of **2c** (84%), bp 109–110° (1 mm), mass spectrum (70 eV) *m/e* 198 M$^+$.

Anal. Calcd for $C_9H_{10}OS_2$: C, 54.51; H, 5.08; S, 32.34. Found: C, 54.49; H, 5.07; S, 32.34.

Acetyl *p*-Tolyl Disulfide (2d).—This disulfide was prepared by treating **1** (5.0 g, 45 mmol) with *p*-thiocresol (5.6 g, 45 mmol) in ether (40 ml). After reflux, work-up, and distillation, 7.8 g (87%) of product was obtained, bp 114–116° (1 mm), mass spectrum (70 eV) *m/e* 198 M$^+$.

Anal. Calcd for $C_9H_{10}OS_2$: C, 54.51; H, 5.08; S, 32.34. Found: C, 54.59; H, 5.06; S, 32.30.

Decomposition of 1.—Spontaneous decomposition of **1** in carbon tetrachloride was followed by nmr at room temperature. After 7 days 27% of **1** was changed to acetyl chloride, and formation of acetylthiosulfenyl chloride was not observed.

Reaction of Acetylthiosulfenyl Chloride with Anisole.—A solution of acetylthiosulfenyl chloride (4.1 g, 29 mmol) in methylene chloride (20 ml) was added dropwise to a cooled (−20°) solution of anisole (3.2 g, 29 mmol) in methylene chloride (30 ml). The system was stirred for 40 hr at room temperature and then heated under reflux for 2 hr. Distillation of the solvent and unreacted anisole gave a yellow liquid (4.3 g). Glpc indicated the presence of **2a** (17%), di-*p*-anisyl sulfide (2%), and di-*p*-anisyl disulfide (42%).

Reaction of 1 with Acetyl *p*-Anisyl Sulfide.—A solution of **1** (0.4 g, 3.3 mmol) and acetyl *p*-anisyl sulfide (0.6 g, 3.3 mmol) in methylene chloride (5 ml) was stirred at room temperature. After 60 hr the yield of **2a** was determined as 44% by glpc. Subsequent refluxing of the reaction mixture for 2 hr caused an increase in the yield up to 47%. Gradual coloring was observed when potassium iodide was added to the reaction mixture, suggesting that **1** still remained in the system.

Registry No.—**1**, 6405-82-9; **2a**, 31570-54-4; **2b**, 31570-55-5; **2c**, 31171-99-0; **2d**, 14227-19-1; **4**, 31570-58-8; **5**, 31570-59-9; anisole, 100-66-3; *m*-xylene, 108-38-3; toluene, 108-88-3; phenol, 108-95-2.

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