lowing, where S_t = molar concentration of dithiinium salt (1) and D_t = molar concentration of dithiin (3) at time t.

$$\ln\frac{S_{t_1}}{S_{t_2}} = kN(t_2 - t_1) \qquad (8)$$

Since

$$A_t = \epsilon_S S_t + \epsilon_D D_t \text{ and } D_t = S_{t=0} - S_t,$$

$$A_t = S_t(\epsilon_S - \epsilon_D) + \epsilon_D S_{t=0} \text{ or } S_t = \frac{(A_t - \epsilon_D S_{t=0})}{\epsilon_S - \epsilon_D}$$

Substitution of this latter equation for S_t into eq 8 gives the final rate equation 9.

$$\ln\frac{A_{t_1} - \epsilon_D S_{t=0}}{A_{t_2} - \epsilon_D S_{t=0}} = kN(t_2 - t_1) \qquad (9)$$

Pseudo-first-order plots of ln ($A_t - \epsilon_D\ S_{t=0}$) vs. time were linear to 2–4 half-lives and both the aniline and thioanisole reactions were found to go essentially to completion. Any absorbance due to the nucleophiles was cancelled by placing in the reference beam a solution of nucleophile of exactly the same concentration as that in the reaction solution. All kinetic determinations were made in triplicate with agreement usually better than ±5%.

Stock solutions of the dithiinium salt (1) and the nucleophile were prepared in the bath. The reaction was started by pipetting a known volume of the dithiinium salt solution into a 10-ml volumetric flask and diluting to the mark with the stock nucleophile solution. In the case of the thioanisole series reactions, dry nitrogen was slowly bubbled through the stock solutions cooled in an ice bath for ca. 20 min and through the reaction solution for about 10 min before placing it in the sample cell. The nucleophile concentrations were typically 0.01–0.20 M for the aniline series reactions and 0.2–1.0 M for the thioanisole series reactions. In the case of the aniline series the fivefold ordinate expansion system of the spectrophotometer was used and the calculated rate constant was usually based on the first 15–30% of the reaction. The normal ordinate plot was used for the thioanisole series and the rate constants were based on approximately the first 75% of the reaction.

Derived rate constants are summarized in Table VII, with errors given as standard deviations. The temperature error (±0.3 °C) represents the outer limits of control as measured at the cell block. A time-averaged standard deviation of temperature in the reaction cuvette could not be determined directly, but was necessarily less than ±0.3 °C.

Registry No.—**1,** 17250-79-2; *p*-chloroaniline, 106-47-8; *m*-methylthioanisole, 4886-77-5; dimethylphenylsulfonium tetrafluoroborate, 33613-52-4.

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Reactions of Acyl Thiochlorosulfites

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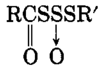
p-Chlorobenzoyl thiochlorosulfite (**1b**) reacted with thiophenols or potassium xanthates to give acyl aryl dithiosulfites (**3**) or acylalkoxythiocarbonyl dithiosulfites (**4**). The reaction of 1 mol of **1b** with 1.5 mol of aniline gave bis-*p*-chlorobenzoyl dithiosulfite (**2b**) and *N*-sulfinylaniline, whereas 1 mol of **1b** with 2 mol of aniline afforded *p*-chlorobenzanilide. Carboxylic acids with **1b** in the presence of triethylamine gave carboxylic anhydrides and **2b**. Reaction of **1** with potassium thiocyanate gave acyl isothiocyanates.

Previously, one of the authors has reported the preparation of diacyl dithiosulfites RCOSS(O)SCOR′ (**2**) and acyl thiochlorosulfites RCOSS(O)Cl (**1**) by the reaction of thiocarboxylic acids and thionyl chloride.[1] Although chlorosulfites ROS(O)Cl are readily prepared from thionyl chloride and alcohols, thiochlorosulfites RSS(O)Cl have not been isolated and their formation has been only postulated as intermediates in the reaction of thionyl chloride and mercaptans.[2] Accordingly, it appeared of interest to investigate the reactions of **1** with various nucleophilic reagents. Aroyl thiochlorosulfites (**1**, R = Ar) are more stable than acyl thiochlorosulfites (**1**, R = alkyl) and some of the former could be isolated as crystalline solids. Reactions were then examined with *p*-chlorobenzoyl thiochlorosulfite (**1b**, R = *p*-ClC_6H_4) which was especially stable and convenient to handle.

Results and Discussion

Thiobenzoic acid or *p*-chlorothiobenzoic acid was allowed to react with thionyl chloride at low temperature to give benzoyl thiochlorosulfite[1] (**1a**) or *p*-chlorobenzoyl thiochlorosulfite (**1b**) in 60–80% yield (eq 1). Acyl thiochlorosulfites were readily hydrolyzed to give diacyl dithiosulfites[1] (**2**) in

Table I[a]

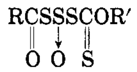


$\mathrm{R\underset{\overset{\|}{O}}{C}S\underset{\overset{\downarrow}{O}}{S}SR'}$

Registry no.	Compd	R	R′	Mp, °C	Yield, %	Ir (KBr), cm^{-1}	
						$\nu_{C=O}$	$\nu_{S\rightarrow O}$
59318-18-2	**3a**	C_6H_5	p-ClC_6H_4	99–102	47	1675	1130
59318-19-3	**3b**	p-ClC_6H_4	C_6H_5	83–87	36	1675	1120
59318-20-6	**3c**	p-ClC_6H_4	p-ClC_6H_4	99–103	64	1675	1130
59318-21-7	**3d**	p-ClC_6H_4	p-$CH_3C_6H_4$	94–100	38	1675	1130

[a] Satisfactory analyses (±0.4% for C, H, and S) were reported for all compounds in table. Ed.

Table II[a]

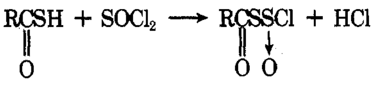


$\mathrm{R\underset{\overset{\|}{O}}{C}S\underset{\overset{\downarrow}{O}}{S}S\underset{\overset{\|}{S}}{C}OR'}$

Registry no.	Compd	R	R′	Mp, °C	Yield, %	Ir (KBr), cm^{-1}	
						$\nu_{C=O}$	$\nu_{S\rightarrow O}$
59318-22-8	**4a**	p-ClC_6H_4	C_2H_5	89–90	25	1675	1150
59318-23-9	**4b**	p-ClC_6H_4	i-C_3H_7	86–88	50	1660	1150
59318-34-0	**4c**	p-ClC_6H_4	n-C_4H_9	60–61	66	1680	1150

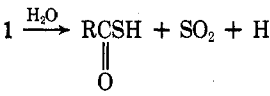
[a] See footnote *a*, Table I.

quantitative yield and no other products were obtained. The result indicates that **1** is initially hydrolyzed to thiocarboxylic acids, which react rapidly with **1**, yielding the final products **2** (eq 2, 3).

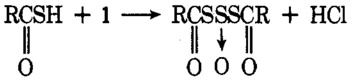


$$\mathrm{R\underset{\overset{\|}{O}}{C}SH + SOCl_2 \longrightarrow R\underset{\overset{\|}{O}}{C}S\underset{\overset{\downarrow}{O}}{S}Cl + HCl} \quad (1)$$

1



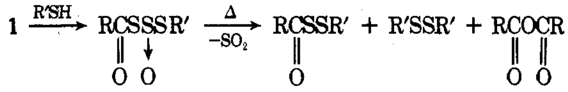
$$\mathrm{1 \xrightarrow{H_2O} R\underset{\overset{\|}{O}}{C}SH + SO_2 + HCl} \quad (2)$$



$$\mathrm{R\underset{\overset{\|}{O}}{C}SH + 1 \longrightarrow R\underset{\overset{\|}{O}}{C}S\underset{\overset{\downarrow}{O}}{S}S\underset{\overset{\|}{O}}{C}R + HCl} \quad (3)$$

2

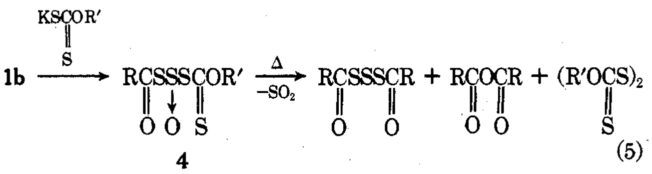
Treatment of **1** with thiophenols gave new mixed anhydrides, acyl aryl dithiosulfites (**3**), in the yields of 36–64% (eq 4). The results are summarized in Table I. By the decomposition of **3c** at the melting point p-chlorobenzoyl p-chlorophenyl disulfide, bis-p-chlorophenyl disulfide, and a small amount of p-chlorobenzoic anhydride were formed with evolution of sulfur dioxide.



$$\mathrm{1 \xrightarrow{R'SH} R\underset{\overset{\|}{O}}{C}S\underset{\overset{\downarrow}{O}}{S}SR' \xrightarrow[-SO_2]{\Delta} R\underset{\overset{\|}{O}}{C}SSR' + R'SSR' + R\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C}R} \quad (4)$$

3

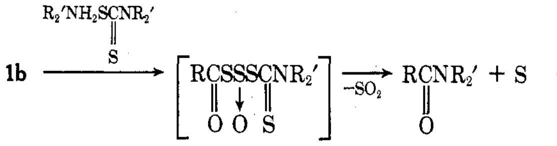
Potassium xanthates reacted with **1b** to give acylalkoxythiocarbonyl dithiosulfites (**4**) in 25–66% yields (eq 5). These new compounds have also interesting mixed anhydride structure. The results are summarized in Table II. By the decomposition of **4a** at the melting point bis-p-chlorobenzoyl trisulfide, p-chlorobenzoic anhydride, and bisethoxythiocarbonyl disulfide were formed with evolution of sulfur dioxide.



$$\mathrm{1b \xrightarrow{K S\underset{\overset{\|}{S}}{C}OR'} R\underset{\overset{\|}{O}}{C}S\underset{\overset{\downarrow}{O}}{S}S\underset{\overset{\|}{S}}{C}OR' \xrightarrow[-SO_2]{\Delta} R\underset{\overset{\|}{O}}{C}SSS\underset{\overset{\|}{O}}{C}R + R\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C}R + (R'O\underset{\overset{\|}{S}}{C}S)_2} \quad (5)$$

4

Dialkylammonium dialkyldithiocarbamates reacted with **1b** at −30 °C to give an oily product. The ir of the oil ($\nu_{C=O}$ 1690 cm^{-1}, $\nu_{S\rightarrow O}$ 1150 cm^{-1}) appeared in a different region from those of **1b** and the spectra of the fingerprint region resembled closely that of dithiocarbamates. So the product was assumed to be acylthiocarbamoyl dithiosulfites (**5**). This product was unstable and gradually decomposed at room temperature to give N-dialkyl-p-chlorobenzamides and sulfur with evolution of sulfur dioxide (eq 6).

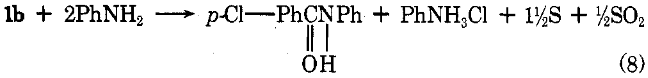


$$\mathrm{1b \xrightarrow{R_2'NH_2S\underset{\overset{\|}{S}}{C}NR_2'} \left[R\underset{\overset{\|}{O}}{C}S\underset{\overset{\downarrow}{O}}{S}S\underset{\overset{\|}{S}}{C}NR_2'\right] \xrightarrow{-SO_2} R\underset{\overset{\|}{O}}{C}NR_2' + S} \quad (6)$$

5

In the reaction of **1b** with aniline the molar ratio of the reagents markedly affected the variety of the products. The reaction of 1 mol of **1b** with 1.5 mol of aniline at low temperature gave bis-p-chlorobenzoyl dithiosulfite (**2b**), N-sulfinylaniline, and aniline hydrochloride, whereas 1 mol of **1b** with 2 mol of aniline afforded p-chlorobenzanilide, sulfur, and aniline hydrochloride. In each case, products were obtained in almost quantitative yields based on the following equations.

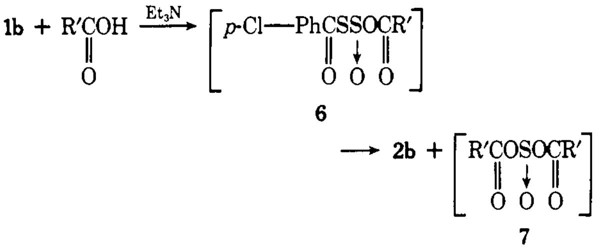
$$\mathrm{1b + 1.5PhNH_2 \longrightarrow \tfrac{1}{2}2b + \tfrac{1}{2}PhNSO + PhNH_3Cl} \quad (7)$$



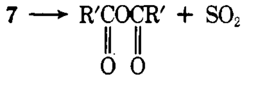
$$\mathrm{1b + 2PhNH_2 \longrightarrow \mathit{p}\text{-}Cl\text{—}Ph\underset{\overset{\|}{O}}{C}\underset{\overset{|}{H}}{N}Ph + PhNH_3Cl + 1\tfrac{1}{2}S + \tfrac{1}{2}SO_2} \quad (8)$$

The reaction of **1b** with 2 mol of diethylamine gave N-diethyl-p-chlorobenzamide, sulfur, and diethylamine hydrochloride with evolution of sulfur dioxide. Triethylamine promoted the decomposition of **1b** at low temperature to give p-chlorobenzoyl chloride.

The reaction of **1b** with carboxylic acids in the presence of triethylamine gave carboxylic anhydrides, bis-p-chlorobenzoyl dithiosulfite (**2b**), and triethylamine hydrochloride with evolution of sulfur dioxide. It seems reasonable to assume that diacyl monothiosulfites (**6**) are initially formed (eq 9) and then disproportionate to give **2b** and diacyl sulfites (**7**) which decompose subsequently to carboxylic anhydrides and sulfur dioxide (eq 9, 10).

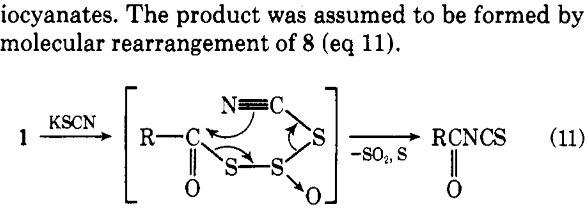


$$\mathbf{1b} + \underset{\text{O}}{\underset{\|}{\text{R}'\text{COH}}} \xrightarrow{\text{Et}_3\text{N}} \underset{\mathbf{6}}{\left[\, p\text{-Cl—Ph}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{S}\underset{\text{O}}{\underset{\downarrow}{\text{S}}}\text{O}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{R}' \,\right]} \longrightarrow \mathbf{2b} + \underset{\mathbf{7}}{\left[\, \text{R}'\underset{\text{O}}{\underset{\|}{\text{C}}}\text{O}\underset{\text{O}}{\underset{\downarrow}{\text{S}}}\text{O}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{R}' \,\right]} \qquad (9)$$



$$\mathbf{7} \longrightarrow \text{R}'\underset{\text{O}}{\underset{\|}{\text{C}}}\text{O}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{R}' + \text{SO}_2 \qquad (10)$$

The reaction of **1** with potassium thiocyanate afforded acyl isothiocyanates. The product was assumed to be formed by intramolecular rearrangement of **8** (eq 11).



8

Reaction of **1** with alcohol at low temperature did not proceed at all. At room temperature decomposition of **1** took place preferentially prior to the reaction with alcohol.

Experimental Section

Infrared spectra were measured with a Hitachi EPI-G2 spectrometer. The NMR spectra were determined on $CDCl_3$ or CCl_4 solutions with a Varian A-60 spectrometer. *p*-Chlorothiobenzoic acid was prepared as previously described.[1] All other reagents were obtained commercially.

Benzoyl Thiochlorosulfite (1a) and *p*-Chlorobenzoyl Thiochlorosulfite (1b). Preparation of **1a** from thionyl chloride and thiobenzoic acid has been reported in the previous paper.[1] Similarly **1b** was obtained: yield 82%; mp 71–74 °C; ir $\nu_{C=O}$ 1665, $\nu_{S\to O}$ 1200 cm^{-1} (CCl_4). Anal. Calcd for $C_7H_4Cl_2O_2S_2$: C, 32.95; H, 1.58; S, 25.13. Found: C, 33.16; H, 1.81; S, 25.02.

Hydrolysis of 1. A solution of 8.7 g (0.034 mol) of **1b** in 40 ml of THF was added dropwise to a stirred 200 ml of water at room temperature during 1 h. After the addition was completed, the white precipitated material was collected by filtration and dried to yield 6.4 g (96%) of bis-*p*-chlorobenzoyl dithiosulfite (**2b**), mp 130 °C.[1] In a similar way **1a** gave dibenzoyl dithiosulfite (**2a**), mp 108 °C,[1] yield 95%.

Reaction of 1 with Thiophenols. A solution of 0.04 mol of thiophenol in 20 ml of ether was added dropwise to a solution of 0.04 mol of **1** in 40 ml of ether at −40 °C during 1 h. Stirring was continued for an additional 2 h and then the temperature of the mixture was allowed to rise to −10 °C. The precipitated material was collected and recrystallized from petroleum ether to yield **3a–d**.

Thermal Decomposition of 3. *p*-Chlorobenzoyl *p*-chlorophenyl dithiosulfite (**3c**, 0.5 g) was heated at 100–110 °C for 1 h under nitrogen atmosphere. After standing at room temperature the mass turned to a mixture of yellow liquid and white solid. Recrystallization of the mixture from *n*-hexane gave 0.05 g of *p*-chlorobenzoic anhydride, mp 192–193 °C (lit. 194 °C). The filtrate was evaporated and the residue was chromatographed on silica gel using CCl_4 as eluent to give 0.1 g of bis-*p*-chlorophenyl disulfide, mp 71 °C (lit. 70–71 °C), and 0.1 g of *p*-chlorobenzoyl *p*-chlorophenyl disulfide, mp 62–65 °C. Anal. Calcd for $C_{13}H_8Cl_2OS_2$: C, 49.53; H, 3.19. Found: C, 49.82; H, 2.96.

Reaction of 1b with Potassium Xanthates. To a solution of 0.03 mol of **1b** in 80 ml of ether, 0.03 mol of powdered potassium xanthate was added little by little with stirring at −30 °C. Stirring was continued for an additional 2 h and then the temperature of the mixture was allowed to rise to −10 °C. Precipitated material was filtered and the filtrate was evaporated. The residual solid was combined with the precipitate and recrystallized from petroleum ether to yield **4a–c**. Since the product was contaminated with **2b** as persistent impurity, recrystallization was required for several times. NMR ($CDCl_3$) of **4a**, δ 1.50 (t, 3, CH_3), 4.79 (q, 2, CH_2), 7.65 (m, 4, phenyl); **4b**, 1.55 (d, 6, CH_3), 5.83 (m, 1; CH), 7.65 (m, 4, phenyl); **4c**, 0.76–2.16 (m, 7, $CH_2CH_2CH_3$), 4.71 (t, 2, $-OCH_2$), 7.63 (m, 4, phenyl).

Thermal Decomposition of 4. *p*-Chlorobenzoyl ethoxythiocarbonyl dithiosulfite (**4a**, 3.2 g) was heated at 90–100 °C for 1 h under nitrogen atmosphere. After standing at room temperature, the mass turned to a mixture of yellow liquid and solid. The mixture was filtered and washed with petroleum ether. Recrystallization of the solid with benzene and *n*-hexane gave 0.5 g of *p*-chlorobenzoic anhydride, mp 193 °C (lit. 194 °C), and 0.7 g of bis-*p*-chlorobenzoyl trisulfide, mp 125–126 °C. Anal. Calcd for $C_{14}H_8Cl_2O_2S_3$: C, 44.80; H, 2.15; S, 25.63. Found: C, 44.92; H, 2.12; S, 25.50. The filtrate was evaporated to give 1.2 g of yellow oil. Distillation of the oil gave 0.5 g of bisethoxythiocarbonyl disulfide: bp 125 °C (0.5 mm) [lit.[3] bp 107–109 °C (0.05 mm)]; ir[4] 1245 (s), 1150 (w), 1110 (m), and 1020 cm^{-1} (s).

Reaction of 1b with Dialkylammonium Dialkyldithiocarbamates. A solution of 8.2 g (0.032 mol) of **1b** in 30 ml of THF was added to a suspension of 5.3 g (0.032 mol) of dimethylammonium dimethyldithiocarbamate in 40 ml of THF at −30 °C during 2 h. Stirring was continued for an additional 3 h and then the temperature of the mixture was allowed to rise to room temperature. Precipitated dimethylammonium chloride was filtered and the filtrate was evaporated under reduced pressure giving **5a** as a light yellow oil. Distillation of the oil gave *N*-dimethyl-*p*-chlorobenzamide: yield 4.1 g (70%); bp 128–130 °C (1.2 mm); mp 57 °C (lit.[5] 59–60 °C); ir $\nu_{C=O}$ 1635 cm^{-1}. Diethylammonium diethyldithiocarbamate reacted similarly with **1b** to give *N*-diethyl-*p*-chlorobenzamide: yield 52%; bp 125 °C (0.5 mm) [lit.[6] 115 °C (0.2 mm)]; ir $\nu_{C=O}$ 1630 cm^{-1}.

Reaction of 1b with a 1.5 Molar Quantity of Aniline. A solution of 9.0 g (0.035 mol) of **1b** in 50 ml of ether was added to a stirred solution of 4.9 g (0.053 mol) of aniline in 20 ml of ether at −30 °C during 1.5 h. After the addition was completed the reaction mixture was stirred at the same temperature for 1 h. Precipitated material was filtered and washed with 20 ml of petroleum ether. The filtrate was evaporated to give *N*-sulfinylaniline which was identified by infrared spectrum.[7] The amount of *N*-sulfinylaniline was estimated as aniline hydrochloride by decomposition with hydrochloric acid, yield 2.1 g (0.016 mol). The previous precipitate was added to 100 ml of water and stirred for 10 min. The white solid was collected and dried under reduced pressure to give 6.8 g (0.017 mol) of bis-*p*-chlorobenzoyl dithiosulfite (**2b**), mp 129–130 °C.[1] The aqueous solution was evaporated under reduced pressure to give 4.3 g (0.033 mol) of aniline hydrochloride.

Reaction of 1b with a 2 Molar Quantity of Amines. A solution of 8.2 g (0.0325 mol) of **1b** in 20 ml of THF was added to a stirred solution of 6.0 g (0.065 mol) of aniline in 50 ml of ether at −30 °C during 1 h. The reaction mixture was stirred at −30 °C for an additional 2 h and then the precipitated material was filtered and the filtrate was evaporated. Residual solid was combined with the precipitate and stirred with 100 ml of water for 10 min. The light yellow solid was collected and recrystallized with EtOH to yield 6.7 g (0.029 mol) of *p*-chlorobenzanilide, mp 194 °C (lit. 194 °C), and 0.6 g of sulfur. The aqueous solution was evaporated to give 4.1 g (0.032 mol) of aniline hydrochloride. Diethylamine (4.1 g, 0.056 mol) reacted similarly with **1b** (7.1 g, 0.028 mol) to give 2.9 g (0.026 mol) of diethylamine hydrochloride, 0.4 g of sulfur, and an oil. The oil was distilled to give 3.8 g (0.018 mol) of *N*-diethyl-*p*-chlorobenzamide, bp 120–121 °C (0.4 mm) [lit.[6] 115 °C (0.2 mm)].

Reaction of 1b with Carboxylic Acids. To a solution of 7.6 g (0.03 mol) of **1b** in 50 ml of ether, a solution of 2.2 g (0.03 mol) of propionic acid in 10 ml of ether was added at −30 °C. After this, a solution of 3.0 g (0.03 mol) of triethylamine in 10 ml of ether was added dropwise over a period of 1 h. Stirring was continued for an additional 1 h and then the temperature of the mixture was allowed to rise to −10 °C. The precipitated material was filtered and the filtrate was distilled to yield 1.2 g (62%) of propionic anhydride, bp 77–78 °C (40 mm). The precipitate was treated with 100 ml of water for 10 min, filtered, and dried to give 5.8 g (99%) of **2b**. The aqueous solution was evaporated to give 4.0 g (97%) of triethylamine hydrochloride. Benzoic acid reacted similarly with **1b** to yield benzoic anhydride (77%) and **2b** (95%).

Reaction of 1 with Potassium Thiocyanate. A solution of 8.0 g (0.031 mol) of **1b** in 30 ml of THF was added to a suspension of 3.0 g (0.031 mol) of KSCN in 70 ml of THF at 0 °C during 2 h. Soon after, the reaction mixture became colored yellow to orange. Stirring was continued for an additional 2 h and then the reaction mixture was filtered. The filtrate was distilled to give 1.5 g (24%) of *p*-chlorobenzoyl isothiocyanate: bp 102–103 °C (0.2 mm) [lit.[8] 114–118 °C (0.35

mm)]; ir $\nu_{C=O}$ 1680, ν_{NCS} 1980 cm^{-1}. In a similar way **1a** gave benzoyl isothiocyanate: bp 130 °C (12 mm) [lit.[8,9] 115 °C (2.2 mm), 133–137 °C (18 mm)]; ir $\nu_{C=O}$ 1685, ν_{NCS} 1970 cm^{-1}; yield 30%.

Registry No.—1a, 41118-54-1; **1b,** 59318-25-1; **5a,** 59318-26-2; thionyl chloride, 7719-09-7; *p*-chlorothiobenzoic acid, 31143-03-0; *p*-chlorobenzoyl *p*-chlorophenyl disulfide, 59318-27-3; bis-*p*-chlorobenzoyl trisulfide, 59318-28-4; bisethoxythiocarbonyl disulfide, 502-55-6; dimethylammonium dimethyldithiocarbamate, 598-64-1; *N*-dimethyl-*p*-chlorobenzamide, 14062-80-7; diethylammonium diethyldithiocarbamate, 1518-58-7; *N*-diethyl-*p*-chlorobenzamide, 7461-38-3; potassium thiocyanate, 333-20-0; *p*-chlorobenzoyl isothiocyanate, 16794-67-5; benzoyl isothiocyanate, 532-55-8; thiophenol, 108-98-5.

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Acid Catalysis in Dimethyl Sulfoxide Reactions. A Generally Unrecognized Factor[1a]

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Strong acids, generated in situ, are effective catalysts for the oxidation of epoxides and benzyl alcohol, the dehydration of tertiary alcohols, and the conversion of acetamide to bis(acetamido)methane in Me_2SO at elevated temperatures (100–190 °C). The reactions are completely inhibited if excess sodium carbonate or other freshly prepared bases (sodium *n*-octoxide or potassium *tert*-butoxide) are present. The acids, the presence of which has usually gone unrecognized, form either by thermolysis of refluxing Me_2SO in air or oxygen or by interaction of free radicals derived from decomposing hydroperoxides or peroxides with Me_2SO. If an efficient radical trapping agent (acrylonitrile) is present during reaction, acid formation is drastically reduced. The acids formed have been isolated by extraction with a solvent-soluble basic ion-exchange resin and identified as sulfuric and methanesulfonic acids.

In many reactions involving dimethyl sulfoxide (Me_2SO) as a reactant and/or solvent without added acid catalysts, the nature of the reactants and products, the experimental conditions, and the obvious analogies to related reactions that normally require strong acids when carried out in other media suggested to us that strong acid catalysis must be playing a critical role. When the present work was initiated in 1966 acid catalysis had neither been demonstrated nor apparently even considered. Since then it has been reported that acid formation may occur in the oxidation of amine salts on prolonged heating in Me_2SO[2] and acid catalysis is involved in the thermolysis of Me_2SO.[3] Beginning with the putative free-radical oxidation of epoxides by Me_2SO,[4] we reinvestigated several of these reactions to attempt to resolve the following questions: (1) Are strong acids formed in situ during these reactions? (2) If acids are formed, how do they originate and can they be isolated and identified? (3) Are the reactions in fact acid catalyzed, failing in the absence of the acids and proceeding normally when the acids are deliberately added?

Results and Discussion

Unrecognized Strong Acid Catalysis in the Me_2SO Oxidation of Epoxides. The reaction of Me_2SO with styrene oxide at 100 °C (molar ratio 6:1) in the presence of a dry air stream was repeated as originally described.[4] The epoxide was consumed and phenacyl alcohol (25%) was formed as reported. Titration of the aqueous extract of the reaction mixture with base, however, revealed the presence of a small quantity of strong acids (2.5×10^{-2} equiv per mole of epoxide originally present). Addition of barium chloride solution showed the presence of sulfate ion. The reaction was then repeated in the presence of *tert*-butyl hydroperoxide (air absent). Again, oxidation of styrene oxide to phenacyl alcohol occurred and strong acids were shown to be formed (ca. $4–6 \times 10^{-2}$ equiv per mole of hydroperoxide). When both reactions were repeated in the presence of an excess of sodium carbonate, *no* phenacyl alcohol was formed; sulfate ion was shown to be present in the aqueous phases.

We[5] and others[6] have shown that the Me_2SO oxidation of epoxides to α-ketols is catalyzed by strong acids. Since we have now demonstrated that strong acids are formed during the Me_2SO oxidation reaction in air and with hydroperoxide, and the oxidation of the epoxide is completely inhibited in the presence of sodium carbonate, we conclude that it is the strong acids formed in these reactions that are the oxidation catalysts and not oxygen or *tert*-butyl hydroperoxide. The mechanism of the acid-catalyzed Me_2SO oxidation of epoxides, therefore, can be assumed to be that proposed earlier by us;[5] the overall process does not involve free radicals except as intermediates in the formation of the acid catalysts, in contrast to an earlier conclusion.[4] We have also demonstrated that the well-known free-radical source, di-*tert*-butyl peroxide, which decomposes in Me_2SO at 100–120 °C, does not produce strong acids in an inert atmosphere and it is not a catalyst for the oxidation of epoxides at that temperature. (At 155 °C, however, even in an inert atmosphere, strong acids do form but that temperature is well above that required in epoxide oxidations.)

Origin of Strong Acids in Epoxide–Me_2SO Reactions. In air, all three components of the reaction mixture (Me_2SO, epoxide, air) are necessary for the formation of the strong acid catalyst. Thus, when styrene oxide is heated in air under the usual reaction conditions but in the *absence* of Me_2SO, no strong acids are produced.[7] When Me_2SO is added to this preoxidized styrene oxide and the reaction is then continued in the *absence* of air, little if any oxidation of epoxide to phenacyl alcohol occurs. Similarly, when air is bubbled