crude product was poured into ice–water and extracted with ether. The organic layer was washed with 10% NaOH and water and dried over Na_2SO_4. Removal of solvent gave 863 mg of residue which was chromatographed on 50 g of silica gel. Elution with 1:1 petroleum ether/benzene gave 645 mg (74%) of 2-heptyl-1,3-dithiane (**2**). An analytical sample was prepared by bulb-to-bulb distillation: ir (neat) 6.82, 7.05, 7.86, 8.47, 10.98 μ; ^{1}H NMR (CCl_4) δ 3.96 (t, 1 H, J = 6.3 Hz, 2-dithiane H).

Anal. Calcd for $C_{11}H_{22}S_2$: C, 60.48; H, 10.15. Found: C, 60.37; H, 10.17.

Preparation of 2-Benzyl-1,3-dithiane. A mixture of 516 mg of 2-phenylethyl phenyl sulfide and 350 mg of NClS in 20 ml of CCl_4 was refluxed, under N_2, for 20 min. After cooling and filtering, the solvent was removed on a rotovac to give 583 mg of chloro sulfide, formed quantitatively by NMR (CCl_4) δ 3.27 (d, 2 H, J = 7.0 Hz) and 5.28 (t, 1 H, J = 7.0 Hz). The product and 1 ml of 1,3-propanedithiol in 20 ml of CH_2Cl_2, under N_2, was cooled to 0 °C and 0.5 ml of BF_3·Et_2O was added. The resulting mixture was stirred at room temperature overnight, then diluted with ether, washed with 10% NaOH solution and water, and dried over Na_2SO_4, and solvent was removed. The residue was chromatographed on silica gel with a 1:1 petroleum ether/benzene mixture to give 344 mg (68%) of the dithiane.[15]

Preparation of 2-Cyanomethyl-1,3-dithiolane. A mixture of 1.039 g of 2-cyanoethyl phenyl sulfide,[16] 0.850 g of NClS, and 25 ml of CCl_4, under N_2, was refluxed for 30 min. The usual workup gave 1.314 g of chloro sulfide, 80% pure by NMR. A mixture of 1.060 g of the crude chloro sulfide, 1.3 ml of 1,2-ethanedithiol, and 1.0 ml of BF_3·Et_2O in 5 ml of CH_2Cl_2 was stirred at room temperature for 24 h. The usual basic workup gave 1.16 g of crude product which was chromatographed on 30 g of silica gel. Elution with 1:1 petroleum ether/benzene followed by bulb-to-bulb distillation gave 405 mg (52%) of 2-cyanomethyl-1,3-dithiolane.[17]

Preparation of 3-Bromopropyl Phenyl Sulfide and 4-Bromobutyl Phenyl Sulfide. A mixture of 22 g of thiophenol, 100 g of 1,3-dibromopropane, 13 g of NaOH, 200 ml of H_2O, 200 ml of PhH, and 1.0 ml of a 40% aqueous solution of tetrabutylammonium hydroxide was stirred at room temperature, under N_2, for 25 min. The organic phase was washed with 10% NaOH solution and water and dried over Na_2SO_4. After removal of solvent, the residue was distilled at 52–54 °C (5.5 mm) to give 61.5 g of 1,3-dibromopropane and at 117–120 °C (1.5 mm) to give 34.6 g (75%) of 3-bromopropyl phenyl sulfide.[18] 4-Bromobutyl phenyl sulfide[18] (bp 112–114 °C at 0.6 mm) was prepared similarly in 76% yield.

Preparation of Octyl Phenyl Sulfide by the Coupling of Grignard Reagents and Bromoalkanes. To a Grignard solution, 1.1 equiv, prepared from 906 mg of bromopentane and 144 mg of Mg in 10 ml of THF, under N_2, and at 0 °C, was added 1 ml of a 0.1 M solution of Li_2CuCl_4[12] and 1.26 g of 3-bromopropyl phenyl sulfide, prepared as above, in 5 ml of THF. After stirring for 2 h at 0 °C and 4 h at room temperature, the mixture was poured into water and extracted with ether. The organic phase was washed with water, 5% NaOH solution, and water and dried over Na_2SO_4. Removal of solvent gave 1.23 g of residue which was carefully chromatographed on 50 g of silica gel. Elution with petroleum ether gave 902 mg (87%, based on unrecovered starting material) of octyl phenyl sulfide[14] and 186 mg of 3-bromopropyl phenyl sulfide. The same product was prepared in 70% yield by a similar coupling reaction between 4-bromobutyl phenyl sulfide and butylmagnesium bromide. Alternately, but less conveniently because of a more complex product mixture, the sulfide could be prepared by the coupling of 3-bromomagnesiopropyl phenyl sulfide and bromopentane.

Acknowledgment. We wish to thank CNPq and CAPES for partial support of this work.

Registry No.—Thiophenol, 108-98-5; 1,3-propanedithiol, 109-80-8; 2-phenyl-1-chloroethyl phenyl sulfide, 59092-73-8; 1,3-dibromopropane, 109-64-8; 3-bromopropyl phenyl sulfide, 3238-98-0; 4-bromobutyl phenyl sulfide, 17742-54-0.

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(6) Aromatic glyoxals and glyoxal derivatives have been prepared from Pummerer rearrangement products under conditions similar to ours, but the starting materials were β-keto sulfoxides: G. A. Russell and J. Mikol, *J. Am. Chem. Soc.*, **88**, 5498 (1966); G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3618 (1969).
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Formation of Thioacetals from Sulfoxides under Pummerer-Type Conditions

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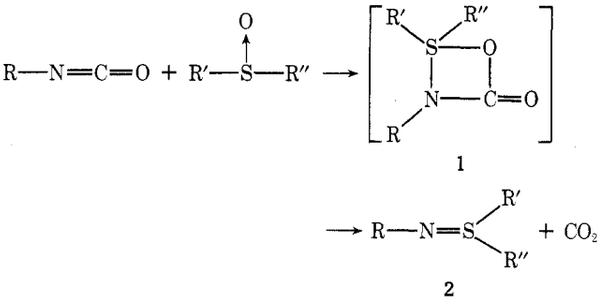
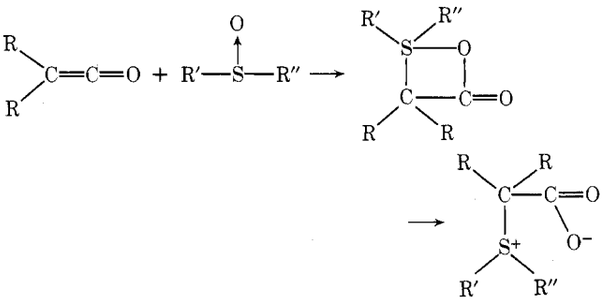
The reaction of isocyanates with sulfoxides has been reported to yield carbon dioxide and sulfilimine derivatives (**2**), presumably via a cyclic intermediate **1**.[1,2] By analogy we anticipated that reaction of sulfoxides with ketenes might lead to **3**. However, when dibenzyl sulfoxide (**4a**) was treated with



1

2



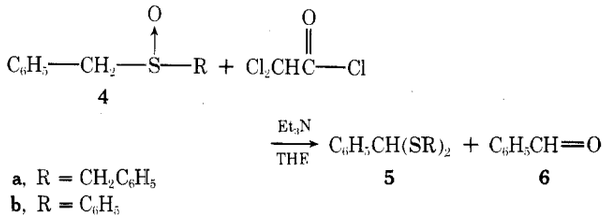
3

Table I. Reaction of Sulfoxides with Acid Chlorides and Anhydrides[i]

Sulfoxide	Acid halide or acid anhydride	Products[a] (% yield[b])
$(C_6H_5CH_2)_2SO$ (4a) (621-08-9)	$CHCl_2COCl$ (79-36-7)	$C_6H_5CH(SCH_2C_6H_5)_2$ (91) (5418-20-2)
4a	$(C_6H_5)_2CHCOCl$ (1871-76-7)	$C_6H_5CH(SCH_2C_6H_5)_2$ (27.4)
4a	AcCl (75-36-5)	$C_6H_5CH(SCH_2C_6H_5)_2$ (5.4); $(C_6H_5CH_2)_2S$ (88)[h] (538-74-9)
4a	Ac_2O[c] (108-24-7)	$C_6H_5CH(SCH_2C_6H_5)_2$ (55.5); $(C_6H_5CH_2)_2S$ (4); $C_6H_5CH_2SCOCH_3$ (6.9) (32362-99-5)
4a	$(CHCl_2CO)_2O$[d] (4124-30-5)	$C_6H_5CH(SCH_2C_6H_5)_2$ (76); $(C_6H_5CH_2)_2S$ (21)
$C_6H_5CH_2SC_6H_5$ (4b) (833-82-9)	$CHCl_2COCl$	$C_6H_5CH(SC_6H_5)_2$ (38); $C_6H_5CH_2SC_6H_5$ (18); (7695-69-4) (831-91-4) $C_6H_5CHClSC_6H_5$ (16.5) (21128-89-2)
4b	Ac_2O[e]	$C_6H_5CH(SC_6H_5)_2$ (80) (7695-69-4)
$C_6H_5SCH_3$ (1193-82-4)	$CHCl_2COCl$[d]	$CH_2(SC_6H_5)_2$[f] (11.8); $(C_6H_5S)_2$ (3) (3561-67-9) (882-33-7)
$C_6H_5SCH_3$ (1193-82-4)	Ac_2O[c]	$C_6H_5SCH_2OCCH_3$ (73) (57440-42-3)
$C_6H_5SCH_3$ (1193-82-4)	$(CHCl_2CO)_2O$[d]	$C_6H_5SCH_2OCCHCl_2$[g] (58.5) (59231-04-8)

[a] Known compounds exhibited physical and spectral parameters in agreement with those of authentic samples. [b] Isolated yield after chromatography. [c] Neat in acetic anhydride, 20 h at 100 °C. [d] Anhydrous THF, 1 equiv of dichloroacetic anhydride, 2 h at 25 °C. [e] Anhydrous *p*-xylene, 12 mmol of acetic anhydride, sealed tube at 140 °C for 6 h. [f] Oil, NMR δ 7.50–7.13 (m, 10), 4.31 (s, 2). Anal. Calcd for $C_{13}H_{12}S_2$: C, 67.20; H, 5.21, Found: C, 67.33; H, 5.28. See ref 10. [g] Anal. Calcd for $C_9H_8N_2O_2S_1$: C, 43.04; H, 3.21. Found: C, 43.10; H, 3.31. [h] The conversion of sulfoxides to sulfides on reaction with acid chlorides is a well-known reaction.[11] [i] Registry no. are in parentheses.

dichloroacetyl chloride in tetrahydrofuran containing triethylamine, the usual conditions for generating dichloroketene in situ, the products were benzaldehyde and the dibenzylmercaptal of benzaldehyde **5a** (91% yield). Although the first

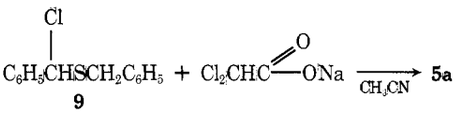


a, R = $CH_2C_6H_5$
b, R = C_6H_5

step in the reaction, under the conditions employed, quite probably is the reaction of the acid chloride with the sulfoxide, the surprising fact is the formation of the mercaptal in high yield rather than the expected α-acyloxy sulfide.

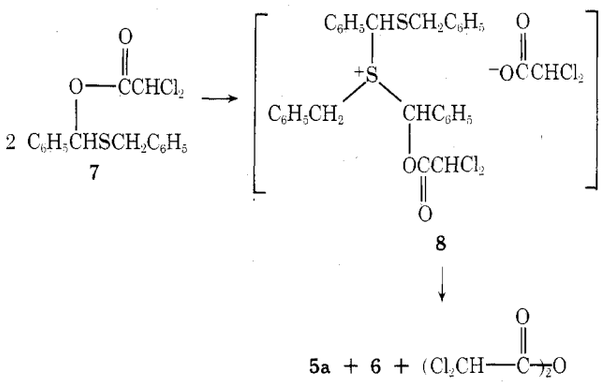
Under the definition suggested by Johnson[3] that the Pummerer reaction embraces a class of reactions involving reduction of a sulfonium sulfur with concomitant oxidation of the α carbon, the above transformation belongs in the broad category of Pummerer reactions. The more usual Pummerer reaction is that of a sulfoxide with a carboxylic anhydride to give an α-acyloxy sulfide[4,5] or α,β-unsaturated sulfides.[6,7] This suggested the possibility that the dibenzylmercaptal of benzaldehyde (**5a**) might be a transformation product of the initially formed α-acyloxy sulfide **7.** In Scheme I a possible mechanism for the conversion of **7** to **5a** is presented. This reaction pathway is analogous to that proposed by Vedejs and Mullins to account for the formation of thioacetal during the thermal rearrangement of a trimethylsilyl sulfoxide.[8]

The key step in the mechanism proposed in Scheme I is the spontaneous reaction of **7** with itself, via an SN1 or SN2 pathway, to give **8.** Subsequent attack on **8** by dichloroacetate anion would then give dichloroacetic anhydride, benzaldehyde (**6**), and the dibenzylmercaptal of benzaldehyde (**5a**). To test the question of whether **7** is stable or whether it would spontaneously undergo conversion to the thioacetal **5a,** an independent synthesis of **7,** involving quite different reaction conditions, was investigated. Treatment of α-chlorobenzyl



benzyl sulfide (**9**) with sodium dichloroacetate in anhydrous acetonitrile, which would be expected to give **7** directly, was found instead to produce the dibenzylmercaptal of benzaldehyde (**5a**) in 70% yield. This result provides good evidence for the intermediacy of α-acyloxy sulfide **7** in the formation

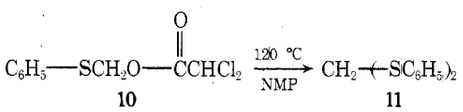
Scheme I



of **5a** and is supportive of the mechanism proposed in Scheme I.

If an α-acyloxy sulfide is first formed during the reaction of a sulfoxide with an acid anhydride or an acid chloride, the question of whether the α-acyloxy sulfide survives intact or is converted to the corresponding thioacetal would be expected to be governed by the usual factors affecting rates of SN1–SN2 reactions. Thus, the nature of the substituents in the sulfoxide as well as the stability of the departing acyloxy anion should play a role. We have carried out several experiments to gain insight regarding these factors and the results are summarized in Table I.

Thus, the reaction of benzyl phenyl sulfoxide (**4b**) with dichloroacetyl chloride under the same conditions as before gave mainly the diphenylmercaptal of benzaldehyde (**5b**) as would be expected. Although methyl phenyl sulfoxide, which lacks benzylic activation, was converted by dichloroacetyl chloride to the corresponding diphenylmercaptal of formaldehyde, the yield was quite poor. Furthermore, the reaction of methyl phenyl sulfoxide with either acetic anhydride or dichloroactic anhydride gave the corresponding α-acyloxy sulfides in good yield. In these instances the reaction conditions were not sufficiently severe for the further conversion of the α-acyloxy sulfides to the acetals. However, when the product, dichloroacetoxymethyl phenyl sulfide (**10**), was heated in *N*-methylpyrrolidone (NMP) at 120 °C for 48 h, it was converted to the diphenylmercaptal of formaldehyde (**11**) in 45% yield.



From these studies it can be concluded that the reaction of sulfoxides with acid halides or acid anhydrides may yield either α-acyloxy sulfides or thioacetals, depending upon the substituents present and the nature of the acid halide or acid anhydride.

Experimental Section

General. Infrared spectra were recorded on a Beckman IR7 spectrophotometer. Solids were recorded as KBr pellets whereas liquids were recorded as thin films on NaCl plates. NMR spectra were recorded on a Varian XL-100 spectrometer using $CDCl_3$ as solvent. Elemental analyses were obtained with a Perkin-Elmer Model 240 C, H, N analyzer. Mass spectra were recorded on a CEC 21-110B mass spectrometer. Melting points were taken with a Dreschel melting point apparatus and are uncorrected. Boiling points were obtained using a micro boiling point tube and are uncorrected. All preparative layer chromatography was done on Analtech silica gel plates.

General Procedure for Reaction of Sulfoxides with Acid Chlorides. A solution of 2 mmol of sulfoxide in 25 ml of anhydrous THF at 25 °C was treated with an equimolar amount of acid chloride. After 15 min 1 equiv of triethylamine was added. The reaction mixture was stirred overnight at 25 °C and the triethylamine hydrochloride was removed by filtration. Concentration of the filtrate under reduced pressure gave an oil which was purified by chromatography.

General Procedure for Reaction of Sulfoxides with Acid Anhydrides. A solution of 2 mmol of sulfoxide in 10 ml of solvent was allowed to react with the appropriate acid anhydride. After completion of the reaction the solution was concentrated under reduced pressure and the resulting oil was purified by chromatography. For specific experimental details see the footnotes of Table I.

Reaction of α-Chlorobenzyl Benzyl Sulfide (9) with Sodium Dichloroacetate. A solution of 0.46 g (2 mmol) of dibenzyl sulfoxide (**4a**) in 10 ml of anhydrous CH_2Cl_2 was added dropwise over a 30-min period to a refluxing solution of 0.17 ml (15% excess) of thionyl chloride in 20 ml of anhydrous CH_2Cl_2. The solution was refluxed for 3 h and concentrated under reduced pressure to give **9** as a slightly yellow oil. A solution of **9** in anhydrous acetonitrile was treated with 0.30 g (2 mmol) of sodium dichloroacetate. A milky precipitate formed immediately. The mixture was stirred for 3 days at 25 °C, the precipitate was removed by filtration, and the filtrate was concentrated under reduced pressure to give a viscous oil. Preparative layer chromatography gave 235 mg (70%) of the dibenzylmercaptal of benzaldehyde (**5a**), mp 59–61 °C (lit.[9] mp 61 °C).

Pyrolysis of Dichloroacetylmethyl Phenyl Sulfide (10). A solution of 120 mg (0.48 mmol) of **10** in 1 ml of anhydrous oxygen-free *N*-methylpyrrolidinone was heated at 120 °C for 48 h. The solution was diluted with 25 ml of $CHCl_3$ and washed with three 15-ml portions of H_2O. The solution was dried ($MgSO_4$) and concentrated under reduced pressure to give a dark oil. Preparative layer chromatography gave 25 mg (45%) of the diphenylmercaptal of formaldehyde (**11**).

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Registry No.—**9**, 51317-73-8; thionyl chloride, 7719-09-7; sodium dichloroacetate, 2156-56-1.

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Cuprous Chloride Catalyzed Alkylations of β Diketones with Methylene Halides

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It has been observed previously that α,ω dihaloalkanes will alkylate dianions of β diketones to form bis-β diketones (eq 1) where $n = 3$ or higher. However, it was also observed that the alkylation reaction did not work for $n = 1$ or 2 under the same conditions.[1] We have recently found that cuprous ions can catalyze coupling reaction of dianions of β diketones that do not readily occur under the conditions or with reagents