The methanolic filtrate from above was evaporated and the black oily residue was dissolved in 35 ml of water and extracted with ether to rid it of phenyl disulfide. The aqueous layer was neutralized with concentrated HCl until an oily precipitate formed. Recrystallization from ethanol afforded 1.83 g (26%) of hairy needles of 1-hydroxy-3-phenylquinoxalin-2-one 4-oxide (9): mp 195–196°; nmr (DMSO) 7.88 (m, 8 H), 8.40 ppm (d, 1 H); ir 3460, 1608, 1590, 1350, 1315, 1250, 1225, 1080, 890, 850, 760, 690 cm^{-1}.

Anal. Calcd for $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.94; N, 11.02. Found: C, 66.36; H, 3.88; N, 11.16.

Reaction of 2-Phenylthio-3-phenylquinoxaline 1,4-Dioxide (8) with Peroxyacetic Acid.—In an erlenmeyer flask were placed 1 g (0.003 mol) of **8** and 30 ml of acetic acid. The solution was warmed to dissolve all the crystals and 6 ml of peroxyacetic acid was introduced. The solution was left for 24 hr and the precipitate that formed was collected and recrystallized from methanol to give 0.4 g (35%) of yellow needles of **10**: mp 231–233°; nmr (CF_3COOH) 7.59 (m, 8 H), 8.40 (m, 4 H), 8.56 ppm (m, 2 H); ir 1360, 1340, 1318, 1270, 1165, 1088, 920, 780, 765, 730, 710, 690 cm^{-1}.

Anal. Calcd for $C_{20}H_{14}N_2O_4S$: C, 63.49; H, 3.57; N, 7.41; S, 8.47. Found: C, 63.40; H, 3.57; N, 7.28; S, 8.61.

Reaction of 1-Hydroxy-3-oxobenzimidazole ($4R_1$) with CS_2.—In an erlenmeyer flask was placed a mixture of 1.59 g (0.01 mol) of $4R_1$, 50 ml of methanol, and 8.6 g (0.1 mol) of CS_2 and the mixture was stirred vigorously until most of the crystals dissolved. The solution was filtered and the solvent was evaporated to dryness. The yellowish oily residue was freed of sulfur by triturating with CS_2. The oil that was left was recrystallized from ethanol to give 0.5 g (37%) of yellow crystals of 1-hydroxybenzimidazole (**11**): mp 210–212° (lit.[9] mp 210–212°); ir 3175, 1590, 1360, 1318, 1230, 1122, 1090, 990, 910, 840, 765, 750, 740, 720 cm^{-1}. Product **11** was identical (mixture melting point, superimposable ir spectra) with an authentic sample prepared by the reduction of o-nitroformanilide with ammonium sulfide.

Reaction of 1-Hydroxy-3-oxobenzimidazole ($4R_1$) with Raney Ni.—In a beaker were placed 1.5 g (0.01 mol) of $4R_1$ and 15 ml of 12% KOH solution. A total of 2 g of Raney Ni was introduced at several intervals of time while warming. The solution was filtered and was neutralized with concentrated HCl. The precipitate that formed was filtered and the neutral filtrate was extracted with ether. The precipitate was boiled with 75 ml of acetone and filtered. The ether extract and acetone filtrate were mixed and the solvent was evaporated. The resulting oil was recrystallized from water to give 0.15 g (13%) of benzimidazole **14**: mp 171–172° (lit.[15] mp 171–172°); ir 3115, 1590, 1480, 1368, 1300, 1276, 1247, 1201, 1137, 1006, 960, 890, 770, 750 cm^{-1}. Product **14** was identical (mixture melting point, superimposable ir spectra) with an authentic sample of benzimidazole.

Reaction of 2-Phenylthio-3-phenylquinoxaline 1,4-Dioxide (8) or 2-Benzenesulfonyl-3-phenylquinoxaline 1,4-Dioxide (10) with Potassium Hydroxide.—In an erlenmeyer flask were placed 0.1 g of either **8** or **10** and 5 ml of 4% methanolic KOH solution. The solution was warmed for 2 hr, neutralized with HCl, and cooled in an ice bath. The crystals that formed were recrystallized from ethanol to give a product that was identical (mixture melting point, superimposable ir spectra) with 1-hydroxy-3-phenylquinoxalin-2-one 4-oxide (**9**).

Reaction of 1-Hydroxy-3-oxobenzimidazole-2-carboxamide ($4R_5$) with HCl.—In a round-bottomed flask equipped with a reflux condenser were placed 0.30 g of $4R_5$, 10 ml of H_2O, and 10 ml of concentrated HCl. The solution was refluxed for 12 hr, cooled, filtered, and neutralized with 40% KOH solution. The crystals that formed were collected, washed with water, and identified as a mixture of 1-hydroxy-3-oxobenzimidazole-2-carboxylic acid and its potassium salt $4R_{11}$.

Registry No.—$4R_1$, 15966-49-1; $4R_2$, 15966-52-6; $4R_3$, 31980-09-3; $4R_4$, 34759-66-5; $4R_5$, 34759-67-6; $4R_6$, 34759-68-7; $4R_7$, 34759-69-8; $4R_8$, 34759-70-1; $4R_9$, 34759-71-2; $4R_{10}$, 34759-72-3; $4R_{11}$, 34759-73-4; **8**, 34759-74-5; **9**, 33074-74-7; **10**, 34759-76-7.

Acknowledgment.—This work was supported, in part, by a Faculty Research Grant from Memphis State University.

(15) Grassi, Gristaldi, and Lambardi, *Gazz. Chim. Ital.*, **25I**, 225 (1885).

Sulfonium Salts. V. The Pummerer Reaction of Dibenzyl Sulfoxide

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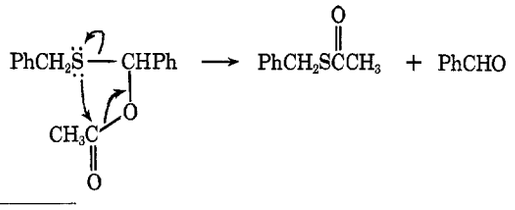
Dibenzyl sulfoxide reacts with acetic anhydride in chloroform and in carbon tetrachloride to provide α-acetoxybenzyl benzyl sulfide as the kinetically controlled product. Longer reaction times led to the products of thermodynamic control, α,α-bisbenzylthiotoluene and benzaldehyde. Benzyl sulfide and benzyl disulfide arise from attack of benzyl mercaptan on the intermediate acetoxysulfonium salt. A competitive kinetic isotope effect of *ca.* 9 characterizes the early stages of the Pummerer reaction.

Benzaldehyde, benzyl mercaptan, benzyl thiolacetate, and α,α-bisbenzylthiotoluene were reported in 1909 by Smythe[2] as the products[3] of the reaction of benzyl sulfoxide with acetic anhydride at 150°. Horner and Kaiser[4] reported that benzyl sulfoxide reacts slowly



with acetic anhydride in chloroform to provide benzaldehyde and benzyl thiolacetate, probably derived from α-acetoxybenzyl benzyl sulfide by an internal rearrangement, but no data supporting the structural assignments were given. The reaction with acetic anhydride has also been compared with the acid-catalyzed transformations of sulfoxides.[5]

Transformations of sulfoxides to α-acetoxy sulfides using acetic anhydride were observed by Pummerer[6] as early as 1909, and this classical reaction[6] bears his name. Since that time the scope of the reaction has been enlarged to encompass a group of similar reactions involving at some point reduction of a sulfonium sulfur atom in an organic molecule with subsequent oxidation of the α-carbon atom. Examples are varied, includ-

(1) Abstracted from a Ph.D. thesis to be submitted by C. J. Strong to the Graduate School of the Polytechnic Institute of Brooklyn in June 1973.

(2) J. A. Smythe, *J. Chem. Soc.*, **95**, 349 (1909).

(3) A recent review erroneously depicts the product as α-acetoxybenzyl benzyl sulfide: G. A. Russell and G. J. Mikol in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, p 157.

(4) L. Horner and P. Kaiser, *Justus Liebigs Ann. Chem.*, **626**, 19 (1959).

(5) D. A. Davenport, D. B. Moss, J. E. Rhodes, and J. A. Walsh, *J. Org. Chem.*, **34**, 3353 (1969).

(6) (a) R. Pummerer, *Ber.*, **42**, 2282 (1909); (b) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 682 (1969).

ing rearrangements of halosulfonium salts to form α-halo sulfides,[7] reactions of sulfoxides with acids to form α-hydroxy sulfides,[7,8] and reactions of methoxysulfonium tetrafluoroborate salts with base to form α-methoxy sulfides.[9]

We initiated our studies on the benzyl sulfoxide–acetic anhydride reaction to provide a direct comparison with the benzyl sulfide–chlorine reaction and to better understand the mechanism of the Pummerer reaction.

Results

Reactions of benzyl sulfoxide with acetic anhydride were conducted at 76° as solutions in deuteriochloroform solution and as suspensions in carbon tetrachloride. Product appearance was followed by quantitative nmr techniques.

The products initially formed were α-acetoxybenzyl benzyl sulfide (I) and acetic acid (II); however, benzyl disulfide (III), benzyl sulfide (IV), benzaldehyde (V), and α,α-bisbenzylthiotoluene (VI) appeared subsequently. After extended reaction periods an additional product, benzyl thiolacetate, was found in small quantities.

The identity of the products II–VI in the mixture

$$\underset{\text{PhCH}_2\overset{\overset{\text{O}}{\|}}{\text{S}}\text{CH}_2\text{Ph}}{} \xrightarrow{\text{Ac}_2\text{O}} \underset{\text{I}}{\text{PhCH(OAc)SCH}_2\text{Ph}} + \underset{\text{II}}{\text{HOAc}} + \underset{\text{III}}{(\text{PhCH}_2\text{S})_2} + \underset{\text{IV}}{(\text{PhCH}_2)_2\text{S}} + \underset{\text{V}}{\text{PhCHO}} + \underset{\text{VI}}{(\text{PhCH}_2\text{S})_2\text{CHPh}}$$

was established by enhancement of appropriate peaks in the nmr spectra caused by addition of authentic materials. Chemical shift assignments are presented in Table I. No benzyl mercaptan was observed in any reaction.

TABLE I

CHEMICAL SHIFTS OF COMPONENTS OF THE REACTIONS OF BENZYL SULFOXIDE WITH ACETIC ANHYDRIDE[a]

Compd	Proton	δ_{DCCl_3}
Benzyl sulfoxide	CH_2	3.75, 4.00[b]
α-Acetoxybenzyl benzyl sulfide	CH_2	3.60, 3.97[b]
	CH	6.92
Dibenzyl sulfide	CH_2	3.55
Dibenzyl disulfide	CH_2	3.58
Benzyl thiolacetate	CH_2	4.10
	CH_3	2.30
Benzaldehyde	CH	10.00

[a] In parts per million downfield from TMS. [b] J = 13 Hz.

α-Acetoxybenzyl benzyl sulfide (I), a compound which has previously eluded detection in the reaction of benzyl sulfoxide with acetic anhydride,[3b,4,8] was isolated in nearly pure form from the reaction mixture.

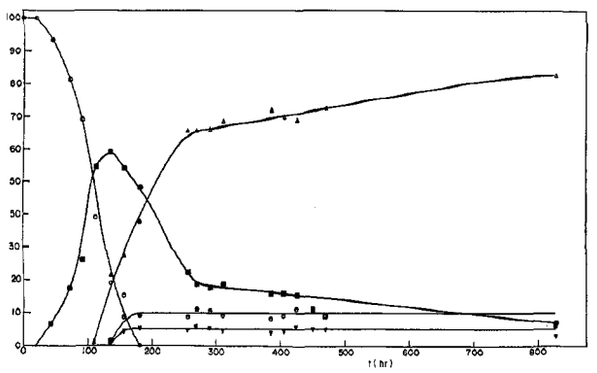


Figure 1.—Reactants and products for the Pummerer reaction of dibenzyl sulfoxide in $DCCl_3$: ■, α-acetoxybenzyl benzyl sulfide; O, dibenzyl sulfoxide; △, α,α-bisbenzylthiotoluene; ●, dibenzyl sulfide; ▼, dibenzyl disulfide.

This was accomplished by neutralizing the acetic acid in a carbon tetrachloride reaction. Solid potassium hydroxide was found to quench the acid-catalyzed conversion of I to V and VI to prevent the hydrolysis of the product. The nmr parameters of I are given in Table I. The mass spectrum of this material did not show a molecular ion, the highest mass peak corresponding to the ion derived by loss of ketene from the molecular ion. In spite of several attempts, the compound could not be obtained analytically pure by chromatographic methods or by distillation.

We have found the reaction of benzyl sulfoxide with acetic anhydride to be highly sensitive to the presence of traces of impurities. Reactions employing carefully recrystallized sulfoxide[10] and carefully cleaned glassware from which traces of acids had been removed by an ammonia rinse followed by a water rinse and oven drying at 120° had half-lives for the disappearance of sulfoxide on the order of a few days (Figure 1). At this time the product was mainly I. Reactions employing slightly impure material in both carbon tetrachloride and deuteriochloroform go to completion in less than 1 day and provide mainly V and VI. We have been unable to obtain sulfoxide dependably free from all trace impurities so that reliable rate data could be obtained. It was observed that addition of either acetic acid or *p*-toluenesulfonic acid resulted in rapid disappearance of starting material and the formation of V and VI. On the other hand, runs in both carbon tetrachloride and deuteriochloroform on several carefully degassed samples showed the reaction velocity and product distribution to be insensitive to dissolved oxygen.

Benzyl sulfoxide-α,α-d_2 for competitive kinetic isotope studies was obtained by oxidation of the sulfide with sodium metaperiodate.[11] In accord with previous observations,[12] no molecular ion for the sulfoxide could be obtained even at low ionizing voltages in the mass spectrometer, the peak at highest mass being that arising through loss of an oxygen atom.

Competitive kinetic isotope effects were obtained at regular intervals for several runs. The data for a

(7) For lead references, see G. E. Wilson, Jr., and M. G. Huang, *J. Org. Chem.*, **35**, 3002 (1970).

(8) H. D. Becker, *ibid.*, **29**, 1358 (1964); J. A. Walsh, *ibid.*, **34**, 3353 (1969).

(9) (a) C. R. Johnson, J. C. Sharp, and W. G. Phillips, *Tetrahedron Lett.*, 5299 (1967); (b) C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, **32**, 1926 (1967).

(10) Some samples of the sulfoxide still contained trace amounts of the sulfone which could not be removed by further recrystallization from water–ethanol mixtures. We could not detect any effect of sulfone on the rate of disappearance of sulfoxide.

(11) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(12) J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, **22**, 3515 (1966).

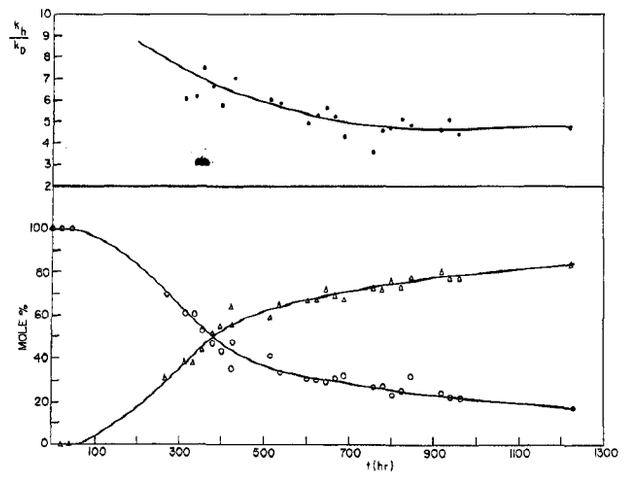
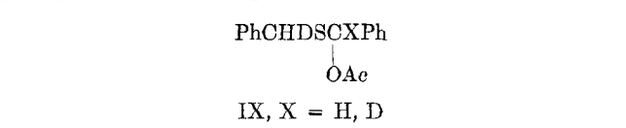


Figure 2.—Competitive kinetic isotope effect (top curve) and reaction progress (bottom curves) as functions of time: Δ, α-acetoxybenzyl benzyl sulfide; O, dibenzyl sulfoxide.

typical run are presented in Figure 2. The competitive kinetic isotope effect was calculated from the integrals of the methine and methylene protons of VII and VIII,

respectively. The integrals of only half of the AB quartet of VIII were used because of interference from the proton signals of III and IV. Values of k_H/k_D were high at the onset of the reaction (see Figure 2) (~9) but the low concentration of product makes the accuracy at this point poor. Toward the end of the reaction the isotope effect decreased to a limiting value of *ca.* 4.5.

Scrambling of the label in α-acetoxy sulfide due to a preequilibrium would give rise to IX in addition to VII



and VIII and this would give rise to peaks for an unsplit proton symmetrically placed within the halves of the AB quartet of the methylene group of VIII. A careful scrutiny of this region using a 220-MHz spectrometer failed to reveal the presence of any such peaks. Under the conditions of the experiment we would expect to be able to observe a 5% contribution from IX.

In all runs the formation of benzyl disulfide takes place only so long as unreacted dibenzyl sulfoxide is present. The concentrations of disulfide and sulfide become constant before the complete disappearance of sulfoxide. The formation of disulfide was also shown to be independent of dissolved oxygen.

Experimental Section

Benzyl Sulfide-α,α-d_2.—This compound was prepared according to the procedure of Wilson and Huang.[7]

Dibenzyl Sulfoxide-α,α-d_2.—To a cold solution of 8.8 g of sodium metaperiodate in 40 ml of water and 40 ml of dioxane was added 8.8 g of benzyl sulfide-α,α-d_2. The resulting slurry was stirred for 72 hr with ice cooling, after which time 100 ml of methylene chloride was added. The methylene chloride layer was separated and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the resulting solid dibenzyl sulfoxide-α,α-d_2, 6.25 g (65% of theory), was recrystallized from ethanol–water to yield colorless plates, mp 131–134°. The absence of sulfide contamination was established by nmr. The compound shows ir absorption at $\nu_{max}^{CHCl_3}$ 1073, 769, and 700 cm^{-1}, and nmr resonances at δ_{CDCl_3} 7.3 (m, 5) and 3.9 ppm (s, 2).

General Procedure for Pummerer Reactions.—Solutions in deuteriochloroform containing 10–15% by weight of benzyl sulfoxide and 1.0–1.5 equiv of freshly distilled, acetic acid free acetic anhydride in sealed nmr tubes were maintained at 76° by total immersion in a constant-temperature bath. The insolubility of benzyl sulfoxide in carbon tetrachloride necessitated that these reactions be initiated as slurries. Solution was achieved as the reaction progressed. In several runs the samples were degassed and sealed under vacuum using three freeze–thaw cycles. In some runs methylene chloride was added as an internal standard for integration. In others, *p*-toluenesulfonic acid, pyridine, or acetic acid was added. The samples were removed at approximately 20-hr intervals and subjected to 60-MHz nmr analysis at ambient temperature.

Oxidation of Benzyl Mercaptan by Benzyl Sulfoxide and Acetic Anhydride.—Sulfone-free benzyl sulfoxide, 10% benzyl mercaptan (1.1 equiv), acetic anhydride (1.2 equiv), and methylene chloride as internal standard in deuteriochloroform solution were sealed in an nmr tube and kept in a constant-temperature bath at 76°. Quantitative conversion of benzyl sulfoxide to benzyl sulfide and conversion of most of the benzyl mercaptan to benzyl disulfide were observed by nmr after 15 hr.

Oxidation of Benzyl Mercaptan with Benzyl Sulfoxide.—A solution of benzyl mercaptan and excess sulfone-free benzyl sulfoxide in deuteriochloroform was sealed in an nmr tube and kept in an oil bath at 76°. After 8 days, no reaction had occurred, but after 2 months 50% of the starting benzyl mercaptan had been converted to benzyl disulfide.

α,α-Bisbenzylthiotoluene.—Benzyl mercaptan and excess benzaldehyde in carbon tetrachloride solution were heated under reflux for 15 hr. The resulting solution was analyzed by nmr and found to contain an aldehyde proton singlet and phenyl multiplet that corresponded to benzaldehyde. An AB quartet (δ 3.58), methinyl singlet (δ 4.50), and phenyl singlet (δ 7.3) were assigned to α,α-bisbenzylthiotoluene.

Oxidation of *p*-Methylbenzyl Mercaptan by Benzyl Sulfoxide and Acetic Anhydride.—To a 12% solution of benzyl sulfoxide in carbon tetrachloride in an nmr tube was added 1 equiv of *p*-methylbenzyl mercaptan and 1.2 equiv of acetic anhydride, and the reaction mixture was maintained at 76° for 18 hr. At this time the sulfoxide had disappeared completely and new peaks were present 213 and 215 Hz downfield from TMS for sulfide and disulfide methylene groups. Separation of the mixture by preparative tlc and analysis of the two fractions by mass spectroscopy showed a molecular ion at *m/e* 214 for the fastest moving spot (dibenzyl sulfide). The slower moving spot, di-*p*-methylbenzyl disulfide, gave no molecular ion, but a peak at *m/e* 137 assignable to p-$CH_3C_6H_4CH_2S^+$.

Discussion

Sulfonium salts bearing one heteroatom attached directly to the sulfur atom are subject to destruction by anions through a variety of routes having roughly comparable free energies of activation. Thus attack of the anion on sulfonium salt IX may in principle take place

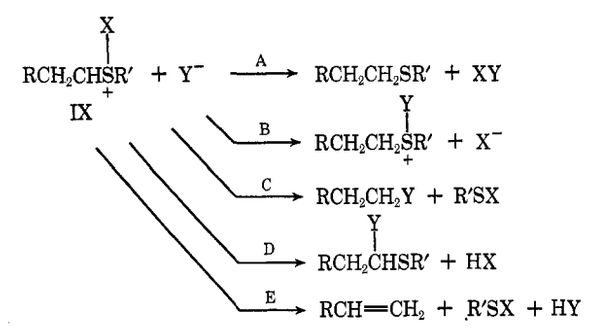


TABLE II

PRODUCT DISTRIBUTION FROM THE REACTIONS OF BENZYL SULFOXIDE WITH ACETIC ANHYDRIDE[a]

Reactants			Time, hr	Sulfoxide	α-Acetoxy sulfide	Sulfide	Disulfide	Thio-acetal	Benzyl-thiol acetate
$(PhCH_2)_2SO$	Ac_2O		20	100					
8% in $CDCl_3$	1.5 equiv		500	18	(max) 52	10	20		
			1000		38	15	30	17	
$(PhCH_2)_2SO$	Ac_2O		20	98	2				
9% in $CDCl_3$	1.2 equiv		130	27	(max) 58	1	2	12	
			1000		5	5	10	70	
$(PhCH_2)_2SO$	Ac_2O	AcOH	20	16	39	13	26	6	
20% in $CDCl_3$	0.6 equiv	0.4 equiv	40			33	66		
$(PhCH_2)_2SO$	Ac_2O	p-CH_3PhSO_3H	20			33	66		
20% in CCl_4	1.8 equiv	Trace							
			20	34	66				
$(PhCH_2)_2SO$	Ac_2O	Pyridine	200	5	66			2	
16% in $CDCl_3$	1.2 equiv	1.5 equiv	1000						
$(PhCH_2)_2SO$	Ac_2O	$PhCH_2SH$	20			100	*b*		
20% in $CDCl_3$	1.2 equiv	1.1 equiv							
$(PhCH_2)_2SO$		$PhCH_2SH$	20	100					
20% in $CDCl_3$		0.7 equiv	2000	66		33	*b*		
$(PhCH_2)_2SOCD_2Ph$	Ac_2O		20	20					
19% in $CDCl_3$	1.9 equiv		300	3	94	1	2		
$(PhCH_2)_2SO$	Ac_2O		20	98	2				
8% in CCl_4	1.5 equiv		1000	14	80	2	4		

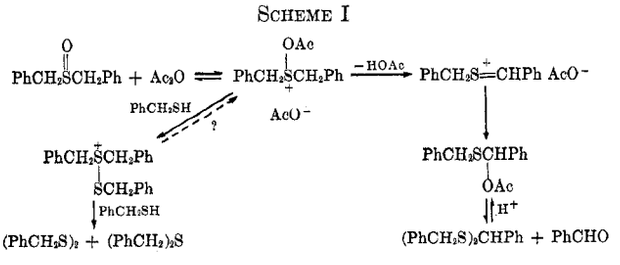
[a] Yields represent the distribution of the sulfur atoms from dibenzyl sulfoxide. Reaction temperatures were 76°. [b] For each mole of benzyl sulfide, one mole of benzyl disulfide is produced; however, this is formed entirely from the added mercaptan.

at the heteroatom (pathway A) to yield a sulfide, at the sulfur atom (pathway B) to yield a new sulfonium salt, at the α-carbon atom (pathway C) to produce products of carbon–sulfur bond cleavage, at the α proton (pathway D) to generate ultimately an α-substituted sulfide or its equivalent, or at the β-hydrogen atom (pathway E) to lead to an olefin and a sulfenyl derivative.

Minor changes in reagents or conditions can divert the entire reaction from one pathway to another. In the reduction of sulfoxides by aqueous hydrogen iodide it is clear that the final step must involve iodide ion attack at the iodine atom of an iodosulfonium salt.[13] By contrast, for the racemization of sulfoxides by hydrogen chloride in aqueous dioxane[14] the chlorosulfonium salt intermediate undergoes displacement by water at the sulfur atom. Chlorination of sulfides in nonnucleophilic solvents, on the other hand, leads to a chlorosulfonium chloride which usually decomposes to produduce α-halo sulfides.[7] Structural changes in the sulfide that stabilize positive charge on the α-carbon atom can lead to partial or total C–S bond cleavage.[7,15]

The reaction of benzyl sulfoxide with acetic anhydride represents a case where several pathways are followed concurrently. At the outset of the reaction (Figure 1) the kinetically favored process for decomposition of the postulated[16] acetoxysulfonium salt intermediate leads to α-acetoxy sulfide, probably by way of a sulfocarbonium ion as shown in Scheme I. In marked contrast to the chlorination of dibenzyl sulfide, in which nucleophilic displacement at the α carbon atom of the chlorosulfonium salt to produce benzyl chloride is an important side reaction throughout, the acetoxy-

SCHEME I



sulfonium salt does not suffer carbon–sulfur bond cleavage to provide benzyl acetate.

The disproportionation of α-acetoxy sulfide takes place in what is probably a series of readily reversible, acid-catalyzed steps to produce the thermodynamically more stable couple, dithioacetal and benzaldehyde. This process must involve the production of benzyl mercaptan as an intermediate at some stage. As expected, the disproportionation becomes more severe as the progress of the Pummerer reaction effects an increase of the acetic acid concentration. Likewise it may be catalyzed by initially added acetic acid or p-toluenesulfonic acid (Table II). Significantly, the disproportionation is greatly retarded by the addition of pyridine (Table II), and this suggests that similar treatment might prove useful to ensure high yields of α-acetoxy sulfides in preparative reactions where disproportionation is troublesome.

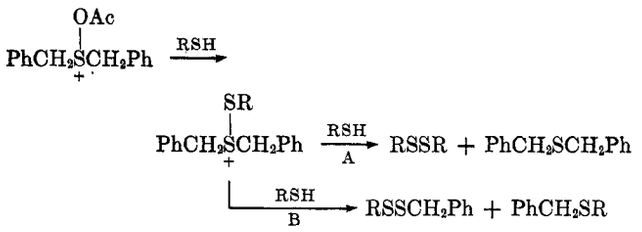
Benzyl mercaptan, when made available in low concentration through the disproportionation reaction, successfully competes with acetate anion to destroy the acetoxysulfonium salt intermediate of the Pummerer reaction, thus forming dibenzyl sulfide and dibenzyl disulfide. This can be seen in Figure 1, where sulfide and disulfide appear concurrently with dithioacetal. In fact, we have shown independently that the addition of benzyl mercaptan to a mixture of sulfoxide and acetic anhydride completely diverts the

(13) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).
(14) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964).
(15) G. E. Wilson, Jr., *ibid.*, **87**, 3785 (1965); (b) K. C. Schreiber and V. P. Fernandez, *J. Org. Chem.*, **26**, 2910 (1961); (c) H. Kwart and J. Miller, *J. Amer. Chem. Soc.*, **80**, 884 (1958).
(16) See, for example, S. Oae and M. Kise, *Tetrahedron Lett.*, 1409 (1967).

reaction toward oxidation of mercaptan to disulfide. By contrast, in the absence of acetic anhydride only a very slow reaction occurs (Table II). Finally, it is interesting to note that the acetoxysulfonium salt does not act as an active ester toward mercaptan; only minor quantities of benzyl thiolacetate are isolated and only after extended reaction periods.

There are two possible loci for attack of a mercaptan on the thiosulfonium salt which must be formed as an intermediate (Scheme II): the α-carbon atom and

SCHEME II

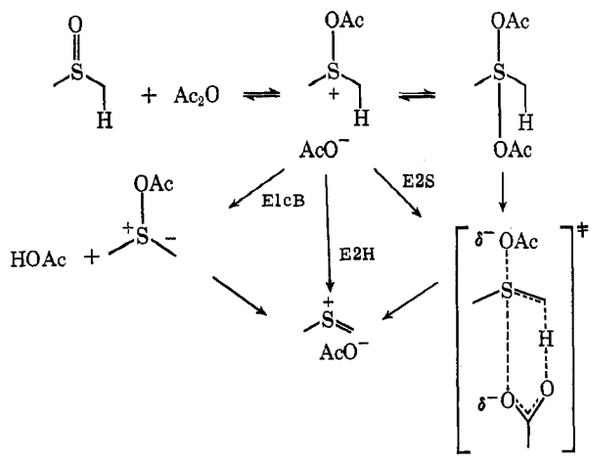


the monoalkylated sulfur atom. In the bromination of dibenzyl sulfide, in which a similar thiosulfonium salt intermediate could be imagined, bromide ion displacement at the α-carbon atom could be excluded as a source of disulfide because of the absence of benzyl bromide as a product in the reaction of benzylsulfenyl bromide with benzyl sulfide.[7] In the present case, the isolation of dibenzyl sulfide and di-*p*-methylbenzyl disulfide from the reaction of *p*-methyl benzyl mercaptan with benzyl sulfoxide and acetic anhydride establishes that mercaptan attack *via* pathway A (Scheme II) has occurred.

Such attack on sulfur is not an unreasonable hypothesis,[17] and it is well known that mercaptides are more thiophilic than nucleophilic. Although attack at the thiol sulfur might not have been expected to be as favorable as attack at the sulfonium sulfur atom, it is clear by inspection that the latter process is a nonproductive one. It may, in fact, be occurring much more rapidly than disulfide formation.

We envision a number of possible means of proton removal from the α-carbon atom (Scheme III) of a

SCHEME III



sulfoxide to produce the sulfocarbonium ion intermediate, all of which would lead to second-order kinetics as observed by Oae and Kise for the Pummerer reaction of aryl methyl sulfoxides.[16] According to current theory,[18,19] the irreversible E1cb route, which should be observed in the aprotic solvents generally used for these reactions, should provide an isotope effect near unity. The remaining three pathways should show $k_H/k_D > 1$, with a magnitude which varies as a function of the transition state symmetry.[20] Those features which make an elimination E1cb-like, an increase in leaving group ability or an increase in base strength, should lead to decreases in the magnitude of k_H/k_D. Since the acetate ion is roughly comparable to chloride ion in leaving ability and of similar basicity in aprotic solvents, we anticipated that the isotope effects on the proton removal steps should both be fairly large. This is indeed the case.

A noncompetitive isotope effect of 2.9 has been previously observed for the Pummerer reaction of aryl methyl sulfoxides by Oae and Kise[16] in a study where they also established that the reaction was overall second order. Noncompetitive isotope effects greater than unity are useful to provide assurance that a proton is being transferred in the slow step of a reaction. Although the k_H/k_D obtained by Oae and Kise[16] is lower than we would have expected, the magnitude depends upon the history of the species undergoing proton transfer. Thus it should reflect the isotope effects on all equilibria preceding proton removal as well as on the slow step. Therefore, we consider our data complementary to that of Oae and Kise,[16] and we consider that taken together they are most compatible with a direct elimination by an E2 or diacetoxysulfurane route not involving an ylide.

The decrease of k_H/k_D as the reaction proceeds is probably attributable to protonation of the acetate oxygen of the acetoxysulfonium salt or diacetoxysulfurane intermediates, thus increasing their leaving group ability.

We do not believe that these results rule out the possibility of an ylide intermediate in other Pummerer reactions, but we expect to observe this alternative pathway only when a strong base is available to remove the α proton. Investigations are in progress to evaluate this possibility.

Registry No.—Dibenzyl sulfoxide, 621-08-9; acetic anhydride, 108-24-7; α-acetoxybenzyl benzyl sulfide, 34804-03-0; dibenzyl sulfoxide-α,α-d_2, 34804-04-1.

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(17) See, for example, J. L. Kice and G. B. Large, *J. Amer. Chem. Soc.*, **90**, 4069 (1968).

(18) Z. Rappoport, *Tetrahedron Lett.*, 3601 (1968).

(19) The validity of k_H/k_D as a measure of the extent of proton transfer in the transition state has recently been questioned: F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 512 (1971).

(20) These arguments are based on an assumed analogy between base-promoted elimination reactions and sulfocarbonium ion formation, both of which involve the loss of HX from vicinal atoms and the development of $p\pi$–$p\pi$ overlap.