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STRUCTURAL EFFECTS UPON COMPETITIVE DECOMPOSITION PATHWAYS OF THIOSULFOXIDE INTERMEDIATES

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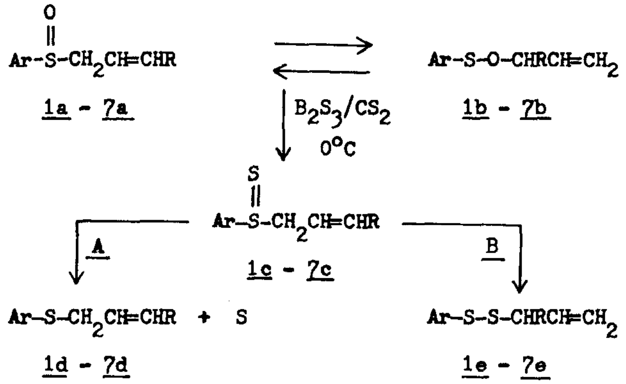
Abstract Mixtures of sulfides and disulfides are obtained upon reaction of boron trisulfide with a series of allyl aryl sulfoxides, with the product distributions dependent upon the structures of the intermediate thiosulfoxides.

In marked contrast to the stability of sulfoxides, the corresponding thiosulfoxides, possessing a terminal sulfur atom in place of oxygen, have never been isolated, nor subjected to direct spectral analysis. Nevertheless, convincing evidence has been presented for their role as intermediates in certain reactions.[1,2] Although thiosulfoxides, which possess a "branched" dipolar structure, are assumed to be less stable than their "linear" isomers, the disulfides,[2,3] the principal factor which precludes their direct study is a pronounced kinetic instability. Thiosulfoxides, however generated,[1,4] are susceptible to a rapid desulfurization to the corresponding sulfides. This instability toward spontaneous desulfurization is a property shared by the somewhat analogous nitrile sulfide intermediates, which also possess a dipolar bond to a terminal sulfur atom.[5,6]

One particularly convenient route to thiosulfoxides involves treatment of sulfoxides with oxygen/sulfur exchange reagents, such as phosphorus pentasulfide (P_4S_{10}) and boron trisulfide (B_2S_3).[4,7] When allylic sulfoxides are employed, two competitive reaction pathways are accessible to the thiosulfoxide intermediates: (2,3)-sigmatropic rearrangement to disulfides as well as spontaneous desulfurization to sulfides. With allyl methyl sulfoxide and allyl phenyl sulfoxide, deoxygenation using either P_4S_{10} or B_2S_3 leads to mixtures of the corresponding disulfides and sulfides, with the latter predominating.[2] Moreover, with the boron trisulfide reagent, the disulfide/sulfide product ratios are appreciably higher, perhaps indicating that thiosulfoxides produced by treatment of sulfoxides with phosphorus pentasulfide are generated in thermal states more highly activated toward rapid desulfurization.

In the present investigation, a series of allyl aryl sulfoxides were prepared and subjected to treatment with boron trisulfide. By correlating modifications in the structures of the allyl and aryl ligands with resulting changes in the disulfide/sulfide product ratios, it has been possible to achieve some understanding of the factors which influence the kinetic stability of thiosulfoxides. If the electronic character of the aryl ligand (Ar) in the sulfoxide (a) contributes to an enhanced thermodynamic stability for the sulfur-sulfur dipolar bond in the corresponding thiosulfoxide (c), it might be expected that the kinetic stability of the thiosulfoxide toward desulfurization (path A) would also be improved, thereby allowing allylic rearrangement (path B) to compete more effectively, with a resultant increase in the disulfide (e)/sulfide (d) product ratio. Similarly, if the stability of the allyl ligand is enhanced by substitution at R, the kinetic stability of the thiosulfoxide toward allylic rearrangement (B) should be improved, allowing desulfurization (A) to compete more effectively,



with a resultant decrease in the disulfide/sulfide product ratio. The results of the reactions, which are summarized in the Table, support these general expectations. A further complexity which must be addressed in several systems is the rapid equilibration of allylic sulfoxides (a) and sulfenates (b) via (2,3)-sigmatropic rearrangement.[8]

Table Deoxygenation of Sulfoxides $ArS(O)CH_2CH=CHR$ with B_2S_3 in CS_2 at 0°C.

Compd	Ar	R	% sulfenate (b)* in equilibrium with sulfoxide (a)	extent of* deoxygenation (%)	% disulfide (e) in product mixture
1a	C_6H_5	H	0	100	30*
2a	p-$O_2NC_6H_4$	H	0	100	40*
3a	p-$CH_3C_6H_4$	H	0	100	3**
4a	p-$CH_3OC_6H_4$	H	0	100	0*,**
5a/b	C_6F_5	H	25	100	0*,**
6b	2,4-$(O_2N)_2C_6H_3$	H	100	0	-
7a	C_6H_5	C_6H_5	0	100	0*

* Estimate based upon ^{1}H-nmr. ** Estimate based upon vpc.

Sulfoxides 1a - 5a and 7a were prepared by oxidation of the corresponding sulfides, using m-chloroperbenzoic acid in dichloromethane at -70°C. Purification was accomplished by column chromatography on silica gel, eluting with hexane/chloroform. The requisite sulfides were prepared by reaction of benzene solutions of the aryl thiols and allyl bromide (cinnamyl bromide for the precursor of 7a) with aqueous sodium hydroxide in the presence of a phase transfer catalyst (adogen 64). Allyl 2,4-dinitrobenzenesulfenate (6b) was prepared by reaction of 2,4-dinitrobenzenesulfenyl chloride and lithium allyl alcoholate in carbon tetrachloride and tetrahydrofuran at 0°C. Analysis of the products by ^{1}H-nmr in carbon disulfide revealed that systems 1a - 4a and 7a were present exclusively in sulfoxide form, whereas the sulfenates 5b and 6b contributed 25% and 100%, respectively, to the equilibrium mixtures for systems 5 and 6.[8]

The deoxygenation reactions were performed in the following manner. A solution of the sulfoxide (1.0 millimole) in 2.0 ml of carbon disulfide was added slowly (ca. 60 sec) to a suspension of boron trisulfide (3.3 millimole) in 2.0 ml of carbon disulfide. Reaction was allowed to continue with vigorous stirring for 25 min at 0°C, whereupon the insoluble reagent was immediately removed by filtration of the reaction mixture through a small, glass wool column. The resulting solution was concentrated somewhat under a stream of nitrogen and then immediately subjected to direct product analysis using a combination of ^{1}H-nmr and vpc on a 1.0 meter apiezon L column. The results reported in the Table are based upon estimates of the product concentrations in solution; they do not represent yields of isolated products.

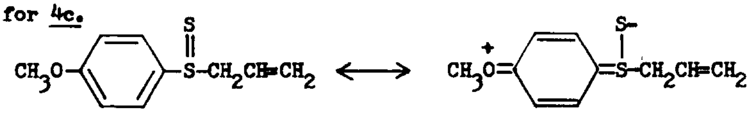
The ^{1}H-nmr spectral measurements were greatly facilitated by application of nmr shift reagents, particularly Eu(fod)$_3$-d$_{30}$. In the absence of the shift reagent, the spectral chemical shifts for the α-allylic protons in a sulfoxide and its corresponding disulfide were often observed to be nearly identical (e. g., δ 3.46 in 1a and 1e). The sulfoxides, however, complex strongly with the shift reagent, causing the allylic protons to exhibit a pronounced downfield shift. The spectra of the disulfides (as well as those of sulfides and sulfenates) remain virtually unchanged by the presence of a shift reagent. The fact that complete deoxygenation occurs in every system except 6b was thus readily verified by spectral analysis.

The contrasting behavior observed with systems 5 and 6 is worth noting. In the pentafluorophenyl system (5), rapid interconversion of the sulfenate (5b) and sulfoxide (5a) permits total deoxygenation, presumably occurring through the sulfoxide isomer. In the 2,4-dinitrophenyl system (6), the equilibrium concentration of sulfoxide (6a) in carbon disulfide must be so negligible that deoxygenation of the sulfenate (6b) is precluded.

In addition to the spectral and chromatographic product analyses, the identification of disulfides 1e - 3e was further supported by the following chemical decomposition. Addition of tri-*n*-butylphosphine to any of the product solutions containing both sulfide and disulfide resulted in the complete disappearance of the component identified as disulfide. Phosphines are known[9] to bring about the conversion of allylic disulfides to sulfides, presumably by desulfurization of the corresponding thiosulfoxides, which are accessible (although at low concentration)[1] through (2,3)-allylic rearrangement.

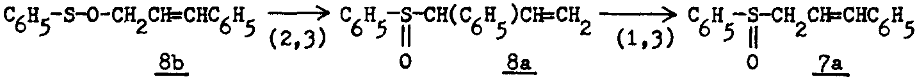
Several trends may be identified from the results summarized in the Table. (1) The stability of the cinnamyl group in thiosulfoxide 7c appears to retard rearrangement to α-phenylallyl phenyl disulfide (7e), thereby assuring dominance for the desulfurization pathway to cinnamyl phenyl sulfide (7d). (2) The reactivity pattern observed within the series 1a - 4a suggests that the kinetic stability of the thiosulfoxides with respect to desulfurization is enhanced by aryl groups which can exert a strong electron-withdrawing effect through resonance (such as the *p*-nitrophenyl in 2c) and diminished by aryl groups whose resonance effect is primarily electron-releasing in nature (such as the *p*-anisyl in 4c). This trend would be expected if the stability of thiosulfoxides is a function of the effectiveness of (p-d)π bonding between the sulfur atoms. This interaction would be diminished, thereby weakening the sulfur-sulfur bond, by "competitive" π-bonding of the central sulfur atom with an electron-releasing aryl ligand, as depicted for 4c using resonance formulas. (3) In spite of the strong, inductive electron-withdrawing effect attributed to the pentafluorophenyl group, it is possible that the apparent instability of the thiosulfoxide (5c) might result from a resonance interaction analogous to that proposed for 4c.

4c



During the course of this study, an attempt was made to synthesize α-phenylallyl phenyl sulfoxide (8a) so as to permit a comparison of its reactivity with the isomeric cinnamyl phenyl sulfoxide (7a). In view of the stability of the cinnamyl group, it was anticipated that cinnamyl phenylsulfenate (8b) might contribute substantially to the sulfoxide/sulfenate equilibrium mixture in this system. The synthesis was approached through direct preparation of the sulfenate (as in 6b) by reaction of benzenesulfenyl chloride and lithium cinnamyl alcoholate in carbon tetrachloride and tetrahydrofuran at -70°C. Upon removal of solvent at low temperature, ^{1}H-nmr analysis revealed the presence of the cinnamyl phenylsulfenate (δ 4.3 (d, J = 6 Hz) for allylic CH_2 in $CDCl_3$). However, upon standing for several hours at room temperature, the sulfenate (8b) underwent complete conversion to cinnamyl phenyl sulfoxide (7a), identical spectroscopically (δ 3.6 (d, J = 6 Hz) for allylic CH_2) to the sample of 7a prepared by oxidation of cinnamyl phenyl sulfide.

Although there is no direct evidence for the intermediacy of α-phenylallyl phenyl sulfoxide (8a) in the rearrangement of 8b to 7a, it is probable that the transformation involves consecutive (2,3)- and (1,3)-allylic rearrangements. Although the concerted character of the (2,3) rearrangement of sulfenates is well established,[8] the nature of the (1,3)-rearrangement in sulfoxides is currently under investigation. A revealing comparison can be made with α,α-dimethylallyl phenyl sulfoxide, which has been reported[10] to undergo the (1,3)-allylic rearrangement readily at 40°C. This system shares with 8a the property that (1,3)-rearrangement generates a sulfoxide which is substantially lower in energy.



$$C_6H_5\text{-S-O-}CH_2CH{=}CHC_6H_5 \xrightarrow[(2,3)]{} C_6H_5\text{-}\underset{\underset{O}{\|}}{S}\text{-}CH(C_6H_5)CH{=}CH_2 \xrightarrow[(1,3)]{} C_6H_5\text{-}\underset{\underset{O}{\|}}{S}\text{-}CH_2CH{=}CHC_6H_5$$

8b 8a 7a

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