

THE INTERMEDIACY OF THIOSULFOXIDES IN
DEOXYGENATION OF SULFOXIDES WITH P_4S_{10}

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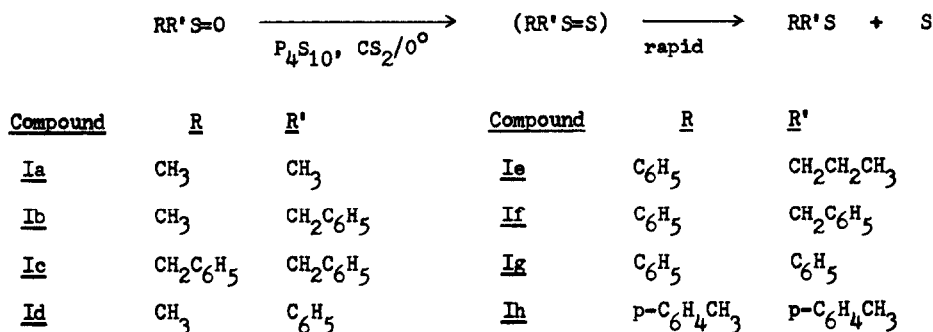
The stability of molecules possessing coordinate covalent bonds to sulfur and phosphorus is well established. Such systems include sulfoxides, sulfilimines, phosphine oxides, phosphine sulfides, and phosphine imines. In view of the stability of these systems, it is perhaps somewhat surprising that the closely analogous thiosulfoxides ($R_2S=S$) have never been successfully isolated. Several systems possessing a formal sulfur-sulfur double bond are, in fact, known, but in each of these special cases, the central sulfur atom is directly bonded to highly electronegative fluorine¹ or oxygen atoms,² which may serve to enhance any (p-d) π conjugative contribution to the sulfur-sulfur bond.

Recent evidence^{3,4} suggests that allylic disulfides exist in equilibrium with undetectably low concentrations of the isomeric thiosulfoxides, interconversion occurring via (2,3)-sigmatropic rearrangement. The direct sulfurization of allylic sulfides to disulfides⁴ has been interpreted⁴ as evidence that thiosulfoxides may also be generated, in extremely low equilibrium concentrations, by the reaction of sulfides with elemental sulfur. These results support the conclusion that thiosulfoxides are thermodynamically unstable with respect to either the isomeric disulfides or to the combination of elemental sulfur with monosulfides.

A principal objective of the present investigation was to examine an effectively irreversible reaction which might be able to generate thiosulfoxides in significant concentrations. Assuming a sufficiently slow rate of spontaneous decomposition under relatively mild conditions, a determination of the kinetic stability (or instability) of the thiosulfoxides would be feasible.

The initial reaction selected for this examination was the treatment of sulfoxides with phosphorus pentasulfide, P_4S_{10} . This reagent has been recently employed to effect conversion of phosphoryl (P=O) to thiophosphoryl (P=S) groups in phosphinates,⁵ phosphonothiolates^{6,7} and phosphine oxides.⁷ A similar transformation might be expected to convert sulfoxides into thiosulfoxides. A series of simple sulfoxides was selected for study.⁸ As depicted in scheme 1, this series includes dialkyl, Ia - Ic, alkyl aryl, Id - If, and diaryl, Ig and Ih, systems. Treatment of the sulfoxides with P_4S_{10} resulted in complete deoxygenation to the corresponding sulfides, with no other products detectable.⁹ Typical conditions consisted of the reaction of equimolar quantities of P_4S_{10} and sulfoxide in carbon disulfide, at a concentration of ca. 0.01 moles of sulfoxide per 30 ml of solvent. The solubility of P_4S_{10} is rather limited, even in carbon disulfide, but continuous stirring of the heterogeneous reaction mixture at 0° C, generally resulted in complete conversion within ten minutes. By extending the reaction time, the transformation was carried out successfully at appreciably lower temperatures. Upon removal of the insoluble residue by filtration through glass wool,

the resulting solutions were analyzed directly⁹ in order to monitor the completeness of the conversion. The sulfides could be isolated in pure form by evaporation of solvent, followed by vacuum kugelrohr distillation or column chromatography on silica gel. The above procedure represents a particularly convenient and inexpensive manner in which to effect the clean deoxygenation of sulfoxides under very mild conditions.¹⁰



SCHEME 1

The sulfoxides were also reduced successfully by a similar treatment with the reagents boron sulfide, B₂S₃, or silicon sulfide, SiS₂.¹¹ Aluminum sulfide, Al₂S₃, was not effective. For several reasons, however, the boron and silicon reagents are somewhat less desirable than phosphorus pentasulfide. They are considerably more expensive, more sensitive to moisture, and their reactions with sulfoxides are slower and produce small amounts of unidentified side products. In marked contrast to the facile reaction of sulfoxides with these sulfide reagents, a selection of sulfones, including dimethylsulfone, methylphenylsulfone, phenylpropylsulfone, and benzylphenylsulfone, were found to be completely inert in a variety of solvents and even at elevated temperatures.¹²

Although the initial impetus for the investigation of these reactions was provided by the pursuit of thiosulfoxides, it is clear that even under the rather mild conditions described above, thiosulfoxides could not be isolated as stable reaction products. Nevertheless, there are several factors which support the suggestion that thiosulfoxides are, in fact, generated as unstable intermediates in the deoxygenation reactions. Phosphorus pentasulfide is not a conventional reducing reagent. In the case of phosphoryl and carbonyl¹³ groups, its function is to effect the replacement of a terminal oxygen atom with sulfur. Sulfoxides presumably react in an analogous fashion, although the initially formed thiosulfoxides undergo a subsequent desulfurization.¹⁴ Consistent with this special "reducing" character, benzyldimethylamine oxide¹⁵ was found to be completely resistant to P₄S₁₀ in carbon disulfide as well as other solvents, and at temperatures up to 100°. This stability contrasts with the relative ease with which amine oxides are deoxygenated by various conventional reducing agents. For example, in sharp contrast to its inertness toward P₄S₁₀, benzyldimethylamine oxide was readily reduced by triphenylphosphine, under conditions which left benzylmethylsulfoxide completely unaffected by this phosphine reducing agent. The sulfoxide, of course, is easily deoxygenated by P₄S₁₀, even at temperatures well below 0°. This markedly different response of amine oxides and sulfoxides toward treatment with the oxygen/sulfur

exchange reagent, P_4S_{10} , may reflect the relative inaccessibility of amine sulfide intermediates, systems which might be expected to exhibit greater instability than thiosulfoxides. Any stabilization of the nitrogen-sulfur bond by (p-d) π conjugation is effectively precluded by the absence of energetically suitable d orbitals on nitrogen, and the formal polarity associated with the bond ($R_2\overset{\delta+}{N}-\overset{\delta-}{S}$) occurs in a direction counter to the inherent electronegativity difference between the elements.

In an attempt to detect the postulated thiosulfoxide intermediates directly, several reactions were monitored by nmr. In a typical procedure, dilute carbon disulfide solutions of P_4S_{10} and dimethylsulfoxide were prepared, mixed rapidly by syringe in an nmr sample tube, and the reaction mixture was immediately frozen in a dry ice/acetone bath. The sample was then transferred to the nmr probe at ambient temperature, and the 1H -nmr spectrum in the methyl region was scanned rapidly and repetitively as the sample thawed. The resulting spectra revealed clearly the rapid emergence of dimethylsulfide accompanied by the simultaneous and complete disappearance of dimethylsulfoxide. No signal which could be attributed to a transient intermediate was observed at any stage, and the reaction was generally complete within two minutes. Similar results were obtained using boron sulfide, although the reactions were somewhat slower. Consequently, it was possible to monitor the early stages of the conversion more thoroughly than with phosphorus pentasulfide.

If dimethylthiosulfoxide is, indeed, an intermediate in this deoxygenation reaction, its lifetime under the above conditions of low temperature and concentration must be measured in seconds, or even fractions of a second. This extreme kinetic instability is consistent with the long and unsuccessful search for stable thiosulfoxides. Direct experimental evidence for the intermediacy of thiosulfoxides in the deoxygenation of sulfoxides would render the above conclusions regarding their kinetic instability more meaningful. An investigation of allylic sulfoxides has, in fact, provided such evidence, and this work is described in the following communication.¹⁶

In view of the current interest in comparing the behavior of related sulfur and selenium systems, an attempt was made to adduce evidence for the intermediacy of various selenium analogs of thiosulfoxides. Unaccountably, these efforts were not successful.¹⁷ Thus, dimethylsulfoxide was found to be unaffected by treatment with P_4Se_{10} , and dimethylselenoxide was quite resistant to either P_4S_{10} or P_4Se_{10} .¹⁸

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