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SYNTHESIS OF OPTICALLY ACTIVE PHENYL BENZENETHIOLSULFINATE BY ASYMMETRIC OXIDATION OF PHENYL DISULFIDE

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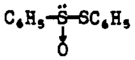
THE demonstration (1,2) that thiolsulfinates, $R-\underset{\downarrow \atop O}{S}-S-R$, and those compounds previously designated as sulfenic anhydrides, R-S-O-S-R, are, in fact, one and the same elevated thiolsulfinates to a position of considerably greater importance in organic sulfur chemistry. In particular, if we accept Vinkler and Klivenyi's (2) assertion that thiolsulfinates are invariably the initial hydrolysis products of sulfenyl halides, the importance of their chemistry to the understanding of various aspects of the chemistry of sulfenyl halides is obvious.

A simple aromatic thiolsulfinate, such as phenyl benzenethiolsulfinate (I), possesses a potential asymmetric center in the sulfinyl group. The availability of optically active aromatic thiolsulfinates



$$C_6H_5-\underset{\downarrow \atop O}{\ddot{S}}-SC_6H_5$$

I

would provide a new and powerful tool for elucidating the mechanisms of certain thiolsulfinate reactions. For such studies it is not necessary that the thiolsulfinate have a high degree of optical purity, only that it possess sufficient rotation to allow accurate polarimetric rate measurements.

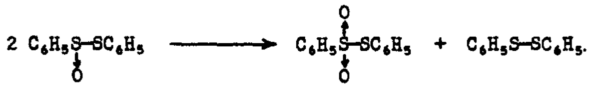
We thought it likely that oxidation of an aromatic disulfide with d-percamphoric acid might lead to a partially optically active aromatic thiolsulfinate, in the same way that partially optically active sulfoxides have been obtained by asymmetric oxidation of unsymmetrical sulfides with the same reagent (3,4). Although the optical purity of the resulting thiolsulfinate would probably be quite low, it might well be large enough, given the frequently sizeable specific rotations of optically pure sulfinyl compounds, for the compound to be employed satisfactorily in polarimetric studies of the type in question. Furthermore, unlike the sulfoxides, where compounds of high optical purity can be easily prepared by other methods (4), no simple alternate route to an optically active aromatic thiolsulfinate suggests itself. As a result, such an asymmetric oxidation, despite its expected low optical yield, could well be the only feasible method for obtaining optically active aromatic thiolsulfinates.

We have found that oxidation of an aromatic disulfide with d-percamphoric acid does indeed represent a simple, convenient method for the preparation of an optically active aromatic thiolsulfinate having a sufficient degree of optical activity for subsequent polarimetric rate measurements.

A solution of phenyl disulfide (0.0218 moles) in chloroform was added with good stirring at -10° to a solution of 0.0218 moles of d-percamphoric acid (5) in the same solvent. After the resulting mixture had stood for 2 hrs. at -5 to -10°, a test for residual peracid was negative. At this point the camphoric acid which had precipitated was filtered off, and the filtrate was washed eight times with 5%

aqueous sodium bicarbonate. It was then washed once with water, dried over anhydrous magnesium sulfate and the chloroform removed under reduced pressure. The residue was recrystallized several times from n-hexane-chloroform, affording pure phenyl benzenethiolsulfinate, m.p. 67-68°, and with infrared and ultraviolet absorption spectra identical with a known sample (6). The yield was approximately 60%. Measurement of the specific rotation showed that the sample of the thiolsulfinate was definitely optically active: $[\alpha]_D^{25}$ +5.11 ± 0.23° (c 5, chloroform).

Proof that all of the optical activity in the thiolsulfinate sample was due to optically active I and not to adventitious impurities was obtained as follows. Aromatic thiolsulfinates undergo disproportionation (equation 1) under a variety of conditions (2,7). If all the



$$2\ C_6H_5\underset{\overset{\downarrow}{O}}{S}\text{-}SC_6H_5 \longrightarrow C_6H_5\overset{\underset{\uparrow}{O}}{\underset{\overset{\downarrow}{O}}{S}}\text{-}SC_6H_5 + C_6H_5S\text{-}SC_6H_5. \qquad (1)$$

optical activity in the thiolsulfinate sample is due to I, subjecting the sample to conditions that lead to disproportionation of I will result in complete loss of optical activity. A sample of the optically active thiolsulfinate was disproportionated under the mildest conditions known to us to induce this chemical change (8), and the specific rotation of the sample was again determined: $[\alpha]_D^{25}$ -0.06 ± 0.26° (c 5, chloroform). This result makes it certain that all the observed optical activity in the original thiolsulfinate sample is due to I.

At present we have no way of determining the optical purity of I produced by this asymmetric oxidation. We suspect, by analogy with sulfoxide systems (3,[illegible]) that it is low. Nonetheless, the specific rotation is large enough so that samples of optically active I produced by this method can easily be employed directly for polarimetric rate studies pertinent to the mechanisms of various thiolsulfinate reactions. (Such studies are in progress and will be reported at a later date.) One thus now has available a new and different system where one can investigate the stereochemistry of reactions involving sulfinyl sulfur.

Although L-cystine($\pm$)-S-monoxide has previously been separated into the two diastereomers, L-cystine-(+)-S-monoxide and L-cystine-(-)-S-monoxide (10), the present case represents, to our knowledge, the first example of an optically active thiolsulfinate in which the sulfinyl group is the sole source of asymmetry in the molecule.

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