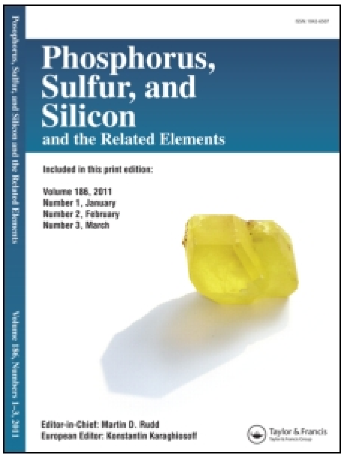

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THIOSULFONATE PREPARATION BY THE THIOSULFINATE/SULFINIC ACID REACTION

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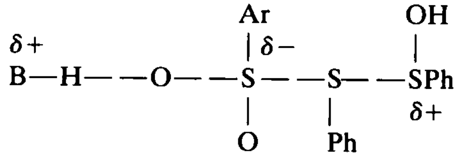
The reaction of thiosulfinates with amine salts of aryl sulfinic acids has been examined for the preparation of thiosulfonates, particularly unsymmetrical derivatives.

Key words: Thiosulfinate; thiosulfonate; sulfinic acid amine salts.

INTRODUCTION

Several methods are available for the preparation of aryl thiosulfonates including the experimentally simple classical method of allowing decomposition of dry sulfinic acid *in vacuo* over a drying agent.[1,2] Other methods using a sulfinic acid involve reaction with a disulfide, which however, may lead to a mixture of derivatives[3] or better, reaction with a thiol in the presence of ethyl nitrite, a more selective process.[4]

The kinetics and mechanism of the thiosulfinate/sulfinic acid process, an interesting reaction between two oxygenated species, have been intensely studied with particular reference to a concomitant acid/base reaction supplemented by catalysis by a small amount of sulfide.[5,6] It was proposed that in a sulfuric/acetic acid medium at 40° reaction proceeded by a base catalyzed attack of the sulfinic acid on a protonated thiosulfinate. This concept was illustrated in an expression summarizing steps in the reaction as:



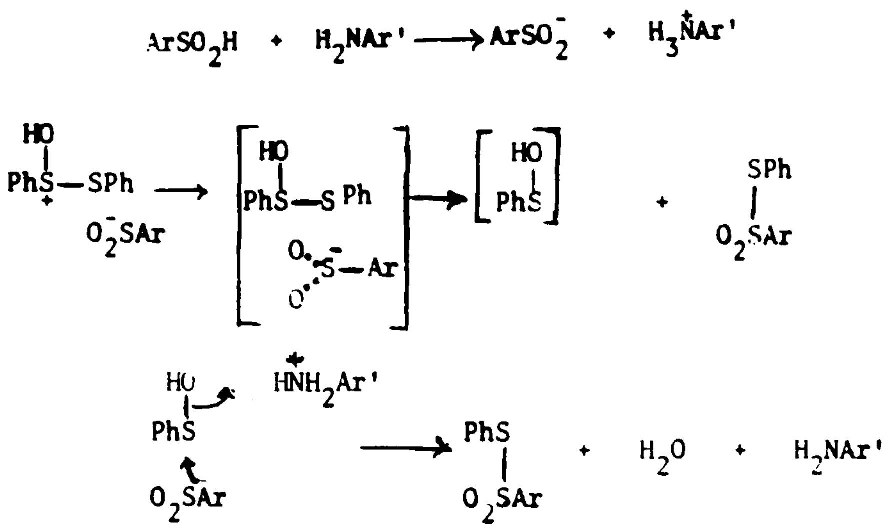
$$\begin{array}{ccccc} & & \mathrm{Ar} & & \mathrm{OH} \\ \delta+ & & |\,\delta- & & | \\ \mathrm{B{-}H{-}{-}} & \mathrm{O{-}{-}} & \mathrm{S{-}{-}{-}} & \mathrm{S{-}{-}} & \mathrm{SPh} \\ & & | & | & \delta+ \\ & & \mathrm{O} & \mathrm{Ph} & \end{array}$$

Thus the process is dependent on the nucleophilicity of the sulfur atom of the sulfinate.

It seemed therefore that use of the amine salt of the sulfinic acid would satisfy two requirements in adding to this property and at the same time in providing a proton carrier.

RESULTS AND DISCUSSION

A mechanism for the reaction under these simpler conditions is shown in the Scheme.



SCHEME

Almost theoretical yields of aryl thiosulfonates were obtained, slightly lower with benzyl derivatives, probably due to longer standing in the medium. Reversibility of a thiosulfonate/amine reaction has been observed.[7] The Scheme suggests a concomitant process for the reaction with induction by the nucleophilicity in the sulfinate ion accompanied by action of the arylamine ion to carry the reaction to completion without implying a termolecular reaction. As indicated in the Scheme where aryl constituents of the thiosulfinate and sulfinic acid are different the reaction becomes suitable for the preparation of unsymmetrical thiosulfonates.

The identity of each thiosulfonate was established by reaction with a thiol. This gives a sulfinic acid, identified as its amine salt, and an unsymmetrical disulfide whose structure in accordance with the selection of the thiol indicates the identity of the sulfonyl group of the thiosulfonate.

$$RSO_2 \cdot SR' + HSR'' \rightarrow RSO_2H + R'S \cdot SR''$$

$$RSO_2H + H_2NR \rightarrow RSO_2^- \cdot H_3N^+R$$

This reaction with a standard thiosulfonate ($PhSO_2SPh$) has been used in the reverse manner for the identification and estimation of thiols. Gas-liquid chromatography of reaction mixtures used for identification show both products on the same chromatogram.[8]

The procedure illustrates the usefulness of thiolsulfinates as starting materials for the preparation of other derivatives, particularly unsymmetricals in the formation of disulfides.

$$RSO \cdot Sr + HSR' \rightarrow [RSOH] + RS \cdot SR'$$

$$[RSOH] + HSR' \rightarrow H_2O + RS \cdot SR'$$

A feature common to reaction of a thiosulfinate with both sulfinic acids and thiols is that the sulfenyl sulfur is the initial point of attack by the reagent and that both sulfur atoms appear in the product.

EXPERIMENTAL

Materials were prepared by standard methods—thiosulfinates by condensation of a sulfinyl chloride with a thiol,[9] thiosulfonates by decomposition of sulfinic acids[2] also used for the preparation of amine salts[10] Benzyl benzylthiosulfonate was prepared by the oxidation of the disulfide with hydrogen peroxide.[11]

Thin layer chromatography was performed using impregnated kieselguhr G plates (0.5 mm) (i) with 3% V/V phenoxyethanol in acetone and *n*-heptane saturated with phenoxyethanol as developing solvent and (ii) with 3% v/v liquid paraffin in acetone with methanol/water 70/30 as developing solvent.

Thiosulfinate/amine sulfinate reactions.

(a) For symmetrical phenyl benzenethiosulfonate: Phenyl benzenethiosulfinate (0, 234 g, 1×10^{-3} M and *p*-toluidine benzenesulfinate (0.498 g, 2×10^{-3} M) in chloroform (50 ml) were allowed to stand in the dark for 3 hr. Solvent was removed *in vacuo* at room temperature and replaced with ether (30 ml) which was washed successively with 0.5 M hydrochloric acid (50 ml) and water (2 × 10 ml). Removal of solvent from the dried solution ($CaCl_2$) gave phenyl benzenethiosulfonate (0, 456 g, 91%). Recrystallization from light petroleum (bp. 40/60°)/chloroform gave pure material mp. 36° with infrared spectrum and tlc R_f value identical with those of reference material.

(bi) Unsymmetrical phenyl *p*-toluenethiosulfonate. In a similar manner phenyl benzenethiosulfinate (0, 148 g, 6.5×10^{-4} M) and *p*-toluidine-*p*-toluenesulfinate (0.341 g, 1.3×10^{-3} M) gave phenyl *p*-toluenethiosulfonate (0.302 g, 90%). Recrystallization from light petroleum/chloroform gave pure material mp. 75° (lit[12] 74°) (Found: C, 59.15; H, 4.89; Calc. for $C_{13}H_{12}O_2S_2$—C, 59.09; H, 4.54)

Structure. To the thiosulfonate (0.132 g, 5×10^{-4} M) in ether (1 ml) was added *p*-thiocresol (0.062 g, 5×10^{-4} M) in ether (5 ml). After standing in the dark for 5 min aniline (0.0465 g, 5×10^{-4} M) was added and the resulting precipitate of aniline *p*-toluenesulfinate separated by filtration, had mp 118° undepressed by admixture with reference material, and with identical infrared spectrum. Removal of solvent from the mother liquor gave a residue of phenyl *p*-tolyl disulfide with tlc R_f value (system ii) identical with that of reference material. Removal of solvent under reduced pressure from the acid extract and washings gave toluidine hydrochloride (0, 139 g, 77%). Recrystallization from ether/ethanol gave pure material mp. 242°, from which the acetylated amine had mp. 146°. Mp's were not depressed on admixture with the respective reference materials whose IR spectra were identical with those of the experimental derivatives as appropriate.

(bii) *p*-Tolyl benzenethiosulfonate. In a similar manner *p*-tolyl-*p*-toluenethiosulfinate (0.66 g, 2.5×10^{-3} M) with *p*-toluidine benzenesulfinate (1.233 g, 5×10^{-3} M) gave *p*-tolyl benzenethiosulfonate (1.124 g, 84%) with mp. 54° (lit[4] 54°) (found: C, 58.92; H, 4.73 Calc, for $C_{13}H_{12}O_2S_2$— —C, 59.09; H, 4.54). Treatment with thiophenol and aniline as described above gave aniline benzenesulfinate mp. 131° undepressed on admixture with reference material and with identical infrared spectrum. *p*-Tolyl phenyl disulfide was also recovered.

(biii) Benzyl *p*-toluenethiosulfonate. By the same procedure benzyl benzylthiosulfinate (0.10 g, 3.8×10^{-4} M) with *p*-toluidine-*p*-toluenesulfinate (0.20 g, 7.6×10^{-4} M) gave, after standing overnight, benzyl *p*-toluenethiosulfonate (0.128 g, 60%) mp. 60° (lit,[12] 60°).

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