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## THIOSULFONIC S-ESTERS—III\*. A CONVENIENT PREPARATION OF AROMATIC SULFIDES

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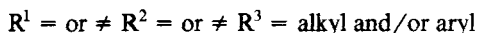
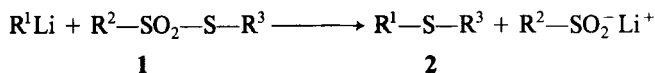
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The nucleophilic attack of alkyl- and aryl-lithium compounds at the sulfenyl sulfur atom in thiosulfonic S-esters performs a convenient synthesis of aromatic sulfides which are obtained cleanly and in generally excellent yields. Considering that recently we have reported a ready preparation of thiosulfonic S-esters from sulfonyl chlorides, this sulfidation reaction completes an interesting general procedure for converting the latter to any symmetrical or unsymmetrical sulfides.

### INTRODUCTION

The chemistry of sulfides is a subject of current interest and the synthesis of diaryl sulfides and aryl alkyl sulfides, which cannot be prepared conveniently by electrophilic substitution with sulfur-containing electrophiles, has been the major objective of several newly reported procedures.<sup>1</sup>

Now, we wish to report that the reaction of metalated aromatic as well as aliphatic compounds with either alkanethiosulfonates or arenethiosulfonates can be exploited conveniently to achieve alkylthiolated and arylthiolated aromatics in a very simple and clean manner and with nearly quantitative yields.



The sharp reactivity of the sulfenyl sulfur atom in thiosulfonates toward nucleophiles is very well known.<sup>2</sup>

The reaction of moderately stable carbanions with thiosulfonates was employed first by Smiles<sup>3,4</sup> in his structure proofs of these esters, thought to be disulfoxides before his work. The reaction was reinvestigated later by Woodward and Pachter<sup>5,6</sup> with the development of trimethylenedithiol ditosylate as a methylene group blocking agent.

Since the early work by Smiles, thiosulfonates have been utilized extensively in organic synthesis<sup>7</sup> for sulfidation of substrates containing active methylene or methine groups, namely mono- and dicarboxylic esters,<sup>8-10</sup> 1,3-dicarbonyl compounds,<sup>11-18</sup> 1,1-disulfones,<sup>19-22</sup> ketones<sup>23,24</sup> and other miscellaneous substances.<sup>25,26</sup>

However, to the best of our knowledge, no literature is available as to the use of thiosulfonates for alkylthiolation and arylthiolation of aromatic compounds. A short

report by Bosscher *et al.*<sup>27</sup> could be considered the only exception. It describes the use of thiosulfonates in the presence of  $\text{AlCl}_3$  to produce sulfides from activated aromatic compounds. In our opinion, however, this procedure does not set an actual precedent since it is based on the attack of a sulfur-containing electrophile on the aromatic substrate rather than the nucleophilic attack of a carbanion on the thiosulfonate as in our case. In addition, the above procedure does not appear to be of great preparative interest.

## RESULTS

Our earliest experiments, were carried out using S-phenyl benzenethiosulfonate (1;  $\text{R}^2 = \text{R}^3 = \text{C}_6\text{H}_5$ ) as a model thiosulfonic S-ester and led to quite satisfactory results. Either alkyl or aryl phenyl sulfides were obtained as unique products, by reaction of 1 ( $\text{R}^2 = \text{R}^3 = \text{C}_6\text{H}_5$ ) with the proper alkyl- or aryl-lithium compound, within seconds, at rather low temperature ( $-10^\circ\text{C}$ ) and in approximately quantitative yield.

The generality of this reaction was explored employing a variety of alkyl- and aryl-lithium compounds in combination with different thiosulfonic S-esters. The results we obtained have been summarized in Table I.

The steric limitations of this reaction were determined using a bulky alkyl-lithium compound, such as *tert*-butyllithium. As a matter of fact thiosulfonic S-esters, when treated with this reagent, still underwent successful reactions (cfr. entries 11 and 12 in the table) although with slightly lower yields owing to the presence of some disulfide ( $\text{R}^2\text{—S—S—R}^3$ ;  $\text{R}^2 = \text{R}^3 = \text{C}_6\text{H}_5$  or *p*-Me- $\text{C}_6\text{H}_4$ ) accompanying the expected sulfide.

The disulfide formation was assumed to be caused by a somewhat slow reaction of *tert*-butyllithium and the starting thiosulfonate which allows some hydrolysis of the lithium reagent and consequent formation of hydroxyl ions in the reaction mixture. This is known<sup>28</sup> to lead to hydrolysis of the thiosulfonates which affords the

TABLE I  
Sulfides from thiosulfonic S-esters

Entry	Sulfide	Starting products	% Yield <sup>a</sup>	Ref.
1	$\text{C}_6\text{H}_5\text{—S—Me}$	$\text{C}_6\text{H}_5\text{—SO}_2\text{S—C}_6\text{H}_5 + \text{MeLi}$	96	30
2	"	$\text{Me—SO}_2\text{S—Me} + \text{C}_6\text{H}_5\text{Li}$	95	30
3	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{—S—Me}$	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{—SO}_2\text{S—C}_6\text{H}_4\text{—}p\text{-Me} + \text{MeLi}$	97	31
4	$\text{C}_6\text{H}_5\text{—S—C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{—SO}_2\text{S—C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{Li}$	94	30
5	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{—S—C}_6\text{H}_5$	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{—SO}_2\text{S—C}_6\text{H}_4\text{—}p\text{-Me} + \text{C}_6\text{H}_5\text{Li}$	93	32
6	$\text{C}_6\text{H}_5\text{—S—}n\text{-Bu}$	$\text{C}_6\text{H}_5\text{—SO}_2\text{S—C}_6\text{H}_5 + n\text{-BuLi}$	96	31
7	"	<i>n</i> -Bu- $\text{SO}_2\text{S—}n\text{-Bu} + \text{C}_6\text{H}_5\text{Li}$	96	31
8	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{—S—}n\text{-Bu}$	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{SO}_2\text{S—C}_6\text{H}_4\text{—}p\text{-Me} + n\text{-BuLi}$	94	33
9	<i>p</i> -MeO- $\text{C}_6\text{H}_4\text{—S—}n\text{-Bu}$	<i>p</i> -MeO- $\text{C}_6\text{H}_4\text{—SO}_2\text{S—C}_6\text{H}_4\text{—}p\text{-OMe} + n\text{-BuLi}$	91	34
10	<i>p</i> -Cl- $\text{C}_6\text{H}_4\text{—S—}n\text{-Bu}$	<i>p</i> -Cl- $\text{C}_6\text{H}_4\text{—SO}_2\text{S—C}_6\text{H}_4\text{—}p\text{-Cl} + n\text{-BuLi}$	93	35
11	$\text{C}_6\text{H}_5\text{—S—}t\text{-Bu}$	$\text{C}_6\text{H}_5\text{—SO}_2\text{S—C}_6\text{H}_5 + t\text{-BuLi}$	89	31
12	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{—S—}t\text{-Bu}$	<i>p</i> -Me- $\text{C}_6\text{H}_4\text{—SO}_2\text{S—C}_6\text{H}_4\text{—}p\text{-Me} + t\text{-BuLi}$	86	31

<sup>a</sup>Yield of pure isolated product; purity  $\geq 95\%$  (as determined by  $^1\text{H-NMR}$  and GLC analysis).

corresponding disulfides. Accordingly, when the reaction was carried out under improved anhydrous conditions (in a dry-box), the amount of disulfide formed was reduced sharply and the sulfide yield increased, thus showing our reaction to be scarcely affected by the steric hindrance of the lithiated species.

Since a wide range of either aliphatic or aromatic compounds can be converted easily to their lithium derivatives, by metalation as well as metal-halogen exchange, this method should find rather broad application for the synthesis of sulfur-substituted aromatics.

Finally, it is worthy of note that the ready preparation of thiosulfonic S-esters we have reported previously,<sup>29</sup> if combined with the present sulfidation procedure, represents an interesting synthetic tool for accomplishing a high-yield two-step conversion of sulfonyl chlorides to any symmetrical and/or unsymmetrical sulfides.

## EXPERIMENTAL

*Preparation of n-butyl phenyl sulfide—General procedure.* To a magnetically stirred hexane solution of *n*-butyllithium (6.0 mmoles), cooled at  $-10^{\circ}\text{C}$  and kept under dry nitrogen, S-phenyl benzenethio-sulfonate (1.0 g; 4.0 mmoles) dissolved in anhydrous  $\text{Et}_2\text{O}$  (10 ml) was added dropwise. The addition was followed immediately by usual work-up of the reaction mixture—treatment with 2N HCl (6 ml), extraction with  $\text{Et}_2\text{O}$  ( $6 \times 30$  ml), washing with water until neutral and evaporation of the organic layers—to afford a crude product which was then chromatographed on silica-gel. Elution with light petrol afforded *n*-butyl phenyl sulfide (0.64 g; 3.8 mmoles; yield 96%) b.p.  $123-5^{\circ}\text{C}/19$  mmHg (lit.<sup>31</sup>  $117-8^{\circ}\text{C}/15$  mmHg).

*n*-Butyl phenyl sulfide was also prepared by reaction of phenyllithium and S-*n*-butyl *n*-butanethio-sulfonate, under the same experimental conditions, with quite comparable yield (cfr. entry 7 in Table I).

In all the cases tested, the reverse addition of lithiated compound to a solution of the proper thiosulfonic S-ester turned out to be only a matter of convenience, the reaction yields being always totally comparable.

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