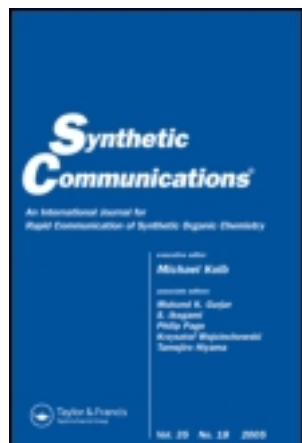


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## Reductive Cleavage of S–S Bond by Zn/AlCl<sub>3</sub> System: A Novel Method for the Synthesis of Sulfides from Alkyl Tosylates and Disulfides

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### ABSTRACT

Alkyl and aryl disulfides are reduced by zinc powder in the presence of AlCl<sub>3</sub> in aqueous media to yield zinc thiolates. This thiolate anion species then react with alkyl tosylates to give sulfides in high to excellent yields.

*Key Words:* Alkyl tosylates; Zn/AlCl<sub>3</sub> system; Reductive cleavage of disulfides; Zinc thiolates; Sulfides.

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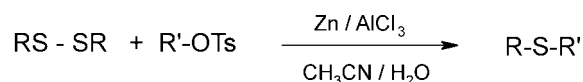
## INTRODUCTION

Historically, the chemistry of sulfides has been relatively well studied. Nevertheless, the chemistry of sulfides is still important from both theoretical and practical viewpoints.<sup>[1]</sup> Sulfides are the starting compounds for the preparations of other sulfur compounds, such as sulfoxides, sulfones, and sulfonium compounds, etc.<sup>[1]</sup> Several procedures for the preparation of sulfides have been reported including, reduction of sulfoxides and sulfones, desulfurization of disulfides, aryllithium or organocuprate addition to thiocarbonyl compounds;<sup>[2,3]</sup> treatment of thiols and alkyl halides with DBU;<sup>[4]</sup> nucleophilic displacement of aryl halides by thiolate ion;<sup>[5]</sup> the treatment of alkyl halides with sodium sulfide,<sup>[6]</sup> thiourea,<sup>[7]</sup> or thiocarbonate,<sup>[8]</sup> the use of *bis*(tributyltin) sulfide as a sulfur transfer agent,<sup>[9]</sup> the reaction of halides with thiosilanes.<sup>[10]</sup> Recently, sulfides have been prepared from thiols using montmorillonite-3-aminopropyltriethoxysilane as a catalyst.<sup>[11]</sup> Also, the synthesis of allyl sulfides from an organosamarium reagent and disulfides has been reported.<sup>[12]</sup> Lu et al.<sup>[13]</sup> synthesized benzyl sulfides via reaction of benzyl bromide with disulfides promoted by Sm/BiCl<sub>3</sub> system in aqueous media. Very recently, we introduced Zn/AlCl<sub>3</sub> system in aqueous media for the preparation of sulfides from disulfides and organic halides.<sup>[14]</sup> Such reactions in aqueous media offer numerous advantages over common reactions in organic solvents.<sup>[13]</sup>

From a synthetic point of view, there are some major limitations to the preparation of sulfides by S–S bond cleavage in disulfides, including: (i) the need for anhydrous organic solvents; (ii) the necessity to prepare an organometallic complex; (iii) strong base catalysis; and (iv) loss of half unit of disulfide.<sup>[13,15]</sup> But, the S–S bond cleavage in disulfides by a Zn/AlCl<sub>3</sub> system, circumvents these problems.

As a part of our ongoing work on Zn/AlCl<sub>3</sub> system, here, we report that alkyl tosylates can react with various disulfides promoted by the above system in CH<sub>3</sub>CN–H<sub>2</sub>O mixed solvent at 65°C to afford sulfides in high to excellent yields (Sch. 1).

A series of symmetrical alkyl and aryl disulfides were treated with various primary alkyl tosylates in the presence of Zn/AlCl<sub>3</sub> system with a molar ratio of disulfide : AlCl<sub>3</sub> : tosylate = 0.5 : 1 : 1.5. The presence of aluminum chloride is quite essential, and in the absence of this Lewis acid, the reaction slows down considerably. The disappearance of zinc powder during the preliminary



*Scheme 1.*



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treatment of disulfides with Zn/AlCl<sub>3</sub> is attributed to the formation of zinc thiolate intermediate<sup>[14]</sup> which further undergoes nucleophilic displacement with alkyl tosylates in the presence of AlCl<sub>3</sub> to afford the sulfide.

The reaction of diaryl disulfides with benzyl tosylates (entries 1–3, Table 1) were rather fast and gave the corresponding benzyl-aryl sulfides in excellent yields. The results also show the need for relatively longer reaction times and sometimes lower yields for symmetrical alkyl disulfides (entries 4, 8, and 9, Table 1).

In conclusion, the present method introduces an alternative with shorter reaction times to the ones reported previously.<sup>[14]</sup> Also, it offers some advantages over earlier reported procedures, in that, it avoids the need to apply thiol, the manipulation of air-sensitive transition metal complexes, and the use of dry solvent, as well as being carried out under mild conditions.

**EXPERIMENTAL**

Disulfides and alkyl tosylates were readily prepared according to the procedures given by Fristad<sup>[22]</sup> and Choudary,<sup>[23]</sup> respectively. All products

**Table 1.** Reaction conditions used and yields of sulfides.

Entry	R	R'	Reaction time (hr)	Yield <sup>a</sup> (%)	M.p. (°C)(obs.)/ M.p. or B.p. (°C, mm) (lit.)
1	Ph	PhCH <sub>2</sub>	4	94	(41–42)/40–42 <sup>[13]</sup>
2	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	3.5	91	(45.5)/45–45.5 <sup>[14]</sup>
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	4	96	(52)/53 <sup>[11]</sup>
4	PhCH <sub>2</sub>	PhCH <sub>2</sub>	8	88	(52)/50 <sup>[16]</sup>
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	PhCH <sub>2</sub>	6	90	(Oil)/130, 5 mm <sup>[14]</sup>
6	Ph	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	11	86	(Oil)/117, 15 mm <sup>[17]</sup>
7	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	9	96	(Oil)/80–82, 1 mm <sup>[14]</sup>
8	PhCH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	9	94	(Oil)/130, 5 mm <sup>[14]</sup>
9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	15	84	(Oil)/187 <sup>[16]</sup>
10	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	5	91	(Oil)/136–7, 10 mm <sup>[18]</sup>
11	Ph	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>	8	99	(Oil)/122–4, 12 mm <sup>[19]</sup>
12	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub>	8	91	(Oil)/175, 12 mm <sup>[14]</sup>
13	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub>	9	86	(Oil)/oil <sup>[20]</sup>
14	Ph	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub>	8	89	(Oil)/oil <sup>[21]</sup>

<sup>a</sup>Yields based on pure isolated products.



were identified by comparison of their spectra and physical data with those of the known samples. IR spectra were recorded using a Shimadzu IR-408 instrument.  $^1\text{H-NMR}$  spectra were determined by a Bruker DRX-500 Avance 500 MHz spectrometer. Melting points were obtained by an Electrothermal 9100 apparatus.

### General Procedure for Preparation of Sulfides

In a 50 mL two-neck flask fitted with a reflux condenser, were placed  $\text{AlCl}_3$  (1 mmol), zinc powder (2 mmol), acetonitrile (10 mL), and disulfide (0.5 mmol). The mixture was stirred at  $65^\circ\text{C}$  for about 2 hr until the zinc powder disappeared; alkyl tosylate (1.5 mmol), and water (2.5 mL) were then added at once to the solution and stirring was continued at that temperature for 3.5–15 hr in air atmosphere. Progress of the reaction was monitored by TLC (eluent: Petroleum ether/EtOAc, 2/1). After completion of the reaction, the solution was filtered and washed with ether. The combined ether/ $\text{CH}_3\text{CN}$  solution was then washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo to give the corresponding sulfide which was purified either by column chromatography using silica gel (Petroleum ether/EtOAc, 2/1), or recrystallized from ethanol.

Selected  $^1\text{H NMR}$  (in  $\text{CDCl}_3$ ) spectral data for product **1**:  $\delta$  3.65 (s, 2H), 7.20–7.50 (m, 10H). **6**:  $\delta$  0.86 (t, 3H,  $J = 7.5$  Hz), 1.22–1.29 (m, 2H), 1.40–1.46 (m, 2H), 2.87 (t, 2H,  $J = 7.8$  Hz), 7.21–7.34 (m, 5H). **10**:  $\delta$  0.91 (t, 3H,  $J = 7.4$  Hz), 1.37–1.48 (m, 4H), 2.90 (t, 2H,  $J = 7.6$  Hz), 7.33 (d, 2H,  $J = 8.0$  Hz), 7.49 (d, 2H,  $J = 8.0$  Hz). **12**:  $\delta$  0.88 (t, 3H,  $J = 7.5$  Hz), 1.21–1.49 (m, 6H), 1.52–1.79 (m, 2H), 2.91 (t, 2H,  $J = 7.6$  Hz), 7.34 (d, 2H,  $J = 8.0$  Hz), 7.44 (d, 2H,  $J = 8.0$  Hz). **14**:  $\delta$  0.87 (t, 3H,  $J = 7.5$  Hz), 1.20–1.48 (m, 6H), 1.50–1.77 (m, 2H), 2.91 (t, 2H,  $J = 7.8$  Hz), 7.23–7.38 (m, 5H).

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