

# Convenient preparation of aryl methyl and aryl phenyl sulfides from arenediazonium tetrafluoroborates and trimethyl(methylthio)- and trimethyl(phenylthio)silanes

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**Dedicated to Professor Gerasimos J. Karabatsos on his 70<sup>th</sup> birthday**

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## Abstract

Aryl methyl and aryl phenyl sulfides were prepared by the reaction of arenediazonium tetrafluoroborates with trimethyl(methylthio)- and trimethyl(phenylthio)silanes, respectively. In the latter case, addition of cupric sulfide was found to increase the yields. The main by-products were protodediazoniated products and diphenyl disulfide, which can be removed by treatment with aqueous sulfide and a base.

**Keywords:** Aryl sulfides, aryl methyl sulfides, arenediazonium tetrafluoroborates, trimethyl(methylthio)- and trimethyl(phenylthio)silanes

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## Introduction

The synthesis of aryl sulfides has attracted continued interest from the time of the discovery of the Ziegler reaction.<sup>2</sup> Many methods have been employed profitably towards their synthesis. Of synthetic significance are reactions such as aluminum bromide induced reactions of aromatic thiols with haloaromatics,<sup>3a</sup> treatment of aryl Grignards or lithiums with sulfur electrophiles,<sup>3b,c</sup> metal induced reduction of disulfides,<sup>3d,e</sup> Ni (II) catalysed arylation arenethiolates using bromoarenes,<sup>3f</sup> photochemical<sup>3g</sup> and electrochemical<sup>3h</sup> S<sub>RN1</sub> reactions of arenethiolates with haloarenes and deoxygenation of sulfoxides.<sup>4</sup>

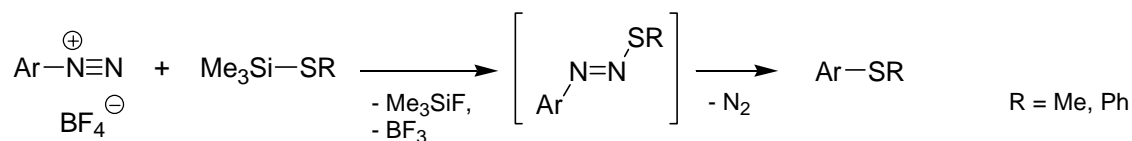
Until recently, the Ziegler reaction has been the main preparative route to diaryl sulfides, because the starting materials are readily available and the procedure is simple. The occurrence of occasional hazards has spurred the introduction of various modifications, mainly to control the accumulation of the aryldiazosulfide, which is a thermally unstable intermediate responsible for

a reported explosion.<sup>5</sup> Petrillo *et al.*<sup>6</sup> have dediazoniated arenediazonium tetrafluoroborates at room temperature in the presence of sodium arylthiolates in dimethylsulfoxide, a solvent supportive of electron transfer processes. They were able to obtain diaryl sulfides in good yields, except from certain haloarenediazonium salts. A recent comprehensive report, in a modified Ziegler reaction, has employed stable and safe arenediazonium *o*-benzenesulfonimides for the preparation of a large number of alkyl aryl and diaryl sulfides using a number of aliphatic and aromatic thiolates under basic conditions.<sup>7</sup>

The stability of arenediazonium tetrafluoroborates makes them attractive arylating agents, they are also easily prepared and stored.<sup>8</sup> Keumi *et al.*<sup>9</sup> have reported that arenediazonium tetrafluoroborates could be readily dediazoniated with trimethylsilyl derivatives such as TMSCl, TMSBr, TMSI and TMSN<sub>3</sub> in dimethylformamide upon warming or at room temperature. Mayr *et al.*<sup>10</sup> have reported that arenediazonium tetrafluoroborates react with allylsilanes to give the allylazo compounds. If the allylic carbon attached to the azo group carries a hydrogen atom, tautomerization occurs with formation of a hydrazone. A novel trifluoromethylthio-dediazoni-ation reaction of arenediazonium salts has been reported using copper trifluoromethylthiolate.<sup>11</sup> We now report that methylthio- and phenylthio-dediazoni-ation of arenediazonium tetrafluoroborates with trimethyl(methylthio)- and trimethyl(phenylthio)silanes to yield the corresponding aryl methyl and aryl phenyl sulfides, respectively, under mild conditions (Scheme 1).

## Results and Discussion

The reactions were carried out in DMF solution at room temperature. The yields of sulfides were found to vary depending on the reactivity and structure of the diazonium salt. Thus, *ortho*-substituted arenediazonium salts reacting with trimethyl(methylthio)silane gave lower yields compared to *para*-substituted ones. Trimethyl(phenylthio)silane reacted similarly. In certain cases, addition of cupric sulfide was found to increase the yield (Table 1). This may involve a single electron transfer (SET)<sup>12</sup> process. In general, the isolated yields of the aryl methyl sulfides were generally lower than that of aryl phenyl sulfides (Table 1). Furthermore, trimethyl(phenylthio)silane tends to form diphenyl disulfide in dimethylformamide even under a nitrogen atmosphere. Therefore, two equivalents of this reagent were used in the reactions with arenediazonium salts. Any disulfide formed can be removed by treatment with 20% aqueous solution of sodium sulfide,<sup>13</sup> and extraction of the resulting thiol by washing with dilute sodium hydroxide solution.



Scheme 1

The suggested mechanism for the reaction involves an initial nucleophilic attack of the sulfanylsilane sulfur atom at the terminal nitrogen atom of the diazonium salt followed by elimination of dinitrogen.<sup>9</sup>

In summary, the developed dediazoniative method compliments other procedures for the preparation of aryl methyl and aryl phenyl sulfides.

**Table 1.** Aryl methyl- and aryl phenyl sulfides from the reaction of arenediazonium tetrafluoroborates and trimethyl(methylthio)silane and trimethyl(phenylthio)silane, respectively

ArN <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	Ar-S-R	Conversion	Isolated yield	Mp or bp/mmHg (mp or bp lit.)	Lit.
Ar	R	[%] <sup>a</sup>	[%]	[°C]	
2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Me		43	63–64 (64–65)	14
2-MeOC <sub>6</sub> H <sub>4</sub>	Me		32	100/1.5 (237/760)	14
4-MeOC <sub>6</sub> H <sub>4</sub>	Me		29	26 (25–26)	14
4-ClC <sub>6</sub> H <sub>4</sub>	Me		31	80/1.4 (104–105/10)	14
3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Me		69	122/3 (125/3.2)	14
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Me		59	65–69 (64)	14
2-FC <sub>6</sub> H <sub>4</sub>	Me		96	75/13 (80/15)	15
Ph	Ph	100	98	96–98/3 (162–163/18)	14
2-FC <sub>6</sub> H <sub>4</sub>	Ph	52	36	115/2.2 (117–120/2.5)	17
4-ClC <sub>6</sub> H <sub>4</sub>	Ph	52/90 <sup>b</sup>	74 <sup>b</sup>	130–133/1.3 (139–140/1.5)	16
4-BrC <sub>6</sub> H <sub>4</sub>	Ph	72	64	23–25 (25–26)	8
3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Ph	46/74 <sup>b</sup>	50 <sup>b</sup>	40–42 (42.5)	14
4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	70/68 <sup>b</sup>	52	118–120/2 (120/2)	3e
2-MeOC <sub>6</sub> H <sub>4</sub>	Ph	0/58 <sup>b</sup>	28 <sup>b</sup>	120/0.2 (154/3)	14

<sup>a</sup> Monitored by GC-MS. <sup>b</sup> With cupric sulfide added to the reaction.

## Experimental Section

**General Procedures.** Arenediazonium tetrafluoroborates were prepared according to literature methods.<sup>8</sup> All products were thoroughly characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and MS analyses. The physical constants (mp and bp) were compared with the data reported in the literature.

**Preparation of aryl phenyl sulfides. General procedure.** A solution of trimethyl(phenylthio)silane (2.0 g, 1.1 mmol) in dimethylformamide (5 mL, spectroscopic grade) was added dropwise over 20 min to a solution of the corresponding diazonium tetrafluoroborate salt (0.55 mmol) in DMF (5 mL) at –10°C (ice/salt mixture bath). The reaction mixture was allowed to warm to room temperature, the solution was stirred with aqueous sodium sulfide solution (10 mL, 20%)

for 12 h and extracted with dichloromethane (3 x 20 mL). The organic layer was washed, in turn, with aqueous sodium hydroxide solution (2 x 30 mL, 20%), water (30 mL), and brine (30 mL). The solvent was removed under vacuum, and the product was isolated by column chromatography on silica with hexane/dichloromethane, or by preparative thin layer chromatography. The compounds were further purified by vacuum distillation or recrystallization. The products were characterized by GC-MS, IR and NMR spectroscopy, and the data agreed with earlier literature data.

**Procedure with cupric sulfide.** A solution of trimethyl(phenylthio)silane (2.0 g, 1.1 mmol) and cupric sulfide (200 mg) in dimethylformamide (5 mL, spectroscopic grade) was added in portions over 20 min to a solution of the corresponding arenediazonium tetrafluoroborate (0.55 mmol) in DMF (5 mL) maintained at  $-10^{\circ}\text{C}$  (by an ice-salt mixture). The reaction mixture was allowed to warm to room temperature. After 18 h the solution was extracted with dichloromethane (2 x 30 mL). After evaporation of the solvent the crude product mixture was dissolved in ethanol (50 mL). Subsequently, aqueous sodium sulfide (10 mL, 20%) was added, and the resulting solution was treated as described above.

**Methyl 4-nitrophenyl sulfide.** A solution of 4-nitrobenzenediazonium tetrafluoroborate (0.5 g, 2.1 mmol) in DMF (5 mL) was added dropwise to a solution of trimethyl(methylthio)silane (0.42 mL, 3 mmol), in dimethylformamide (5 mL) with constant stirring at room temperature. Stirring was continued for one hour, and then the reaction mixture was poured into water (50 mL) followed by extraction with dichloromethane (2 x 30 mL). The solvent was removed under vacuum, and the crude product was purified by column chromatography on alumina with hexane/dichloromethane (1:1) as the eluent. Yield: 0.21g, 59%; colorless crystals, mp 65–69  $^{\circ}\text{C}$  (mp lit.<sup>14</sup> 64  $^{\circ}\text{C}$ ).

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