

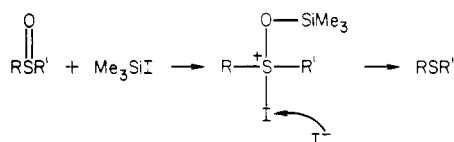
# Synthetic Methods and Reactions. 93.<sup>1</sup> Preparation of Disulfides via Iodotrimethylsilane-Mediated Reductive Dimerization of Sulfonyl Halides

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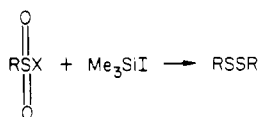
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Iodotrimethylsilane and its equivalents are versatile synthetic reagents which have been used in the cleavage of esters, lactones, carbamates, ethers, etc.<sup>2</sup> We recently reported<sup>3</sup> that sulfoxides are cleanly reduced to the corresponding sulfides on treatment with iodotrimethylsilane.

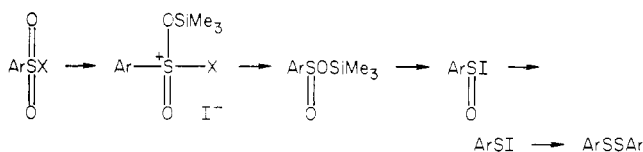


We now report that sulfonyl halides can be similarly deoxygenated with iodotrimethylsilane to yield disulfides in high yield.



Aryl and alkyl sulfonyl chlorides and bromides react rapidly with iodotrimethylsilane at room temperature. Alkylsulfonyl chlorides are less reactive, but at 81 °C, the alkyl disulfides are obtained in good yield. In a typical reaction, the sulfonyl halide was stirred with 5-mol equiv of iodotrimethylsilane in an inert solvent (1,2-dichloroethane, dichloromethane). As the reaction proceeds, iodine is liberated, accompanied by the formation of hexamethyldisiloxane and chlorotrimethylsilane.

We propose that sulfonyl chlorides and bromides are initially reduced to trimethylsilyl sulfinate esters by analogy with the known reaction of sulfonyl chlorides with cyanide,<sup>4</sup> iodide, and other reducing agents.<sup>5</sup> The sulfinate esters can undergo subsequent deoxygenation to yield eventually sulfinyl iodides which couple to the disulfide products.



Sulfinic acids, sulfinic acid salts, alkyl sulfonates, sulfinyl chlorides, and sulfinyl bromides are all reduced rapidly under the reaction conditions to yield the symmetrical disulfides (Table I). By use of only 1 equiv of iodotri-

Table I. Reductive Coupling of Sulfonyl, Sulfinyl, and Sulfinyl Derivatives to Disulfides with Iodotrimethylsilane<sup>a</sup>

substrate	disulfide <sup>b</sup> yield, %
CH <sub>3</sub> SO <sub>2</sub> Cl	100 <sup>c</sup>
CH <sub>3</sub> CH <sub>2</sub> SO <sub>2</sub> Cl	80 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> Cl	98
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> Cl	100
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	89
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Br	90
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	86
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl <sup>d</sup>	79
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl <sup>e</sup>	80
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	100
<i>p</i> -FC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	90
<i>p</i> -FC <sub>6</sub> H <sub>4</sub> SOCl	96
<i>p</i> -FC <sub>6</sub> H <sub>4</sub> SOCl	88
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Na	75
<i>p</i> -FC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Me	89

<sup>a</sup> Isolated yield of reaction at 25 °C for 16 h in methylene chloride. See experimental section for details. <sup>b</sup> All products gave satisfactory melting or boiling points and NMR and IR spectra. <sup>c</sup> Reaction in 1,2-dichloroethane at reflux for 16 h. <sup>d</sup> Me<sub>3</sub>SiCl/NaI in acetonitrile. <sup>e</sup> Me<sub>3</sub>SiSiMe<sub>3</sub>/I<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>.

methylsilane, a fraction of the starting material is reduced completely to the disulfide, implying that subsequent steps are much faster than the initial reaction. Sulfonyl fluorides, sulfonic acids, and their salts and esters<sup>6</sup> are not reduced on treatment with iodotrimethylsilane.

The reaction can also be carried out with iodotrimethylsilane (or its equivalents) generated in situ from either chlorotrimethylsilane/sodium iodide<sup>7</sup> or hexamethyldisilane/iodine.<sup>8,9</sup> More conveniently, we have found that the reaction can be performed by using chlorotrimethylsilane in nonnucleophilic solvents (e.g., methylene chloride, chloroform), using a suspension of sodium iodide in the presence of a phase-transfer catalyst (tetra-*n*-butylammonium iodide).

While this work was in progress, Pinnick et al.<sup>10</sup> have observed that aromatic sulfinate salts yield the corresponding disulfides on reaction with ethyl hypophosphite. Among other reagents, hydrobromic and hydriodic acids<sup>11</sup> have been employed in conjunction with reducing agents to achieve the reductive dimerization of sulfonyl halides and sulfinic acids. Our present work demonstrates the synthetic utility of iodotrimethylsilane as a neutral equivalent for hydriodic acid.

## Experimental Section

All sulfonyl halides, sulfinyl halides, sulfinyl halides, and the silanes were commercially available materials of high purity or were synthesized by standard procedures. NMR and IR spectra were recorded on Varian A56/60 and Perkin-Elmer 297 spectrometers, respectively. Melting points were obtained on a Mettler FP-1 melting-point apparatus and are uncorrected.

**Procedure for Conversion of *p*-Toluenesulfonyl Chloride to *p*-Tolyl Disulfide with Iodotrimethylsilane.** Iodotrimethylsilane (10 g, 50 mmol) was added to a stirred solution of *p*-toluenesulfonyl chloride (1.9 g, 10 mmol) in methylene chloride

(6) Methyl *p*-toluenesulfonate is cleaved by iodotrimethylsilane.

(7) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* 1979, 44, 1247-1251.

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(9) Only a catalytic amount of iodine is required, since the reaction regenerates iodine.

(10) Pinnick, H. W.; Reynolds, M. A.; McDonald, R. T., Jr.; Brewster, W. D. *J. Org. Chem.* 1980, 45, 930-932.

(11) Challenger, F.; Miller, S. A.; Gibson, G. M. *J. Chem. Soc.* 1948, 769-771.

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(2) Olah, G. A.; Narang, S. C.; Salem, G. F.; Gupta, B. G. B. *Synthesis*, in press.

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(4) Corson, F. P.; Pews, R. G. *J. Org. Chem.* 1971, 36, 1654-1659.

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(ca. 25 mL) and stirred under a nitrogen atmosphere for 16 h at room temperature. The dark color of iodine develops almost immediately and iodine crystallizes from the solution as the reaction progresses. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of a saturated solution of sodium thiosulfate. The mixture was extracted with methylene chloride (2 × 50 mL). The extracts were dried over anhydrous magnesium sulfate and the solvent was removed to yield a crude product which was taken up in hexane and filtered through a short silica gel column. Removal of the solvent afforded *p*-tolyl disulfide (1.1 g, 89%), mp 46.0 °C (lit.<sup>12</sup> mp 48 °C).

**Procedure for Conversion of *p*-Toluenesulfonyl Chloride to *p*-Tolyl Disulfide with Chlorotrimethylsilane/Sodium Iodide.** Chlorotrimethylsilane (7.6 g, 70 mmol) was added to a stirred solution of *p*-toluenesulfonyl chloride (1.9 g, 10 mmol) in dry acetonitrile (30 mL). Sodium iodide (12 g, oven dried) was added and the mixture was stirred for 16 h at room temperature under a nitrogen atmosphere. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of sodium thiosulfate. The mixture was extracted with ether (3 × 25 mL) and the combined extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed to yield a crude product which was taken up in hexane and filtered through a short column of silica gel. Removal of the solvent afforded *p*-tolyl disulfide (0.96 g, 79%), mp 46.0 °C (lit.<sup>12</sup> mp 48 °C).

**Procedure for Conversion of *p*-Bromobenzenesulfonyl Chloride to *p*-Bromophenyl Disulfide with Hexamethyldisilane/Iodine.** Iodine (0.25 g, 1.0 mmol) was added to a stirred solution of *p*-bromobenzenesulfonyl chloride (1 g, 4 mmol) and hexamethyldisilane (1.75 g, 12.0 mmol) in methylene chloride (ca. 25 mL) and the mixture was stirred for 16 h at room temperature. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of sodium thiosulfate. The mixture was extracted with methylene chloride (3 × 25 mL) and the extracts were dried over anhydrous magnesium sulfate. The solvent was removed to yield a crude product which was taken up in hexane and filtered through a short column of silica gel. Removal of the solvent gave *p*-bromophenyl disulfide (0.59 g, 80%), mp 95.2 °C (lit.<sup>12</sup> mp 94.5 °C).

**Procedure for Conversion of *p*-Chlorobenzenesulfonyl Chloride to *p*-Chlorophenyl Disulfide with Chlorotrimethylsilane/Sodium Iodide under Phase-Transfer Conditions.** Sodium iodide (15 g, 100 mmol) was suspended in a solution of chlorotrimethylsilane (5.5 g, 50 mmol) in methylene chloride (ca. 50 mL) containing a catalytic amount of tetra-*n*-butylammonium iodide (200 mg). *p*-Chlorobenzenesulfonyl chloride (2.1 g, 10 mmol) was added and the mixture was stirred for 16 h at room temperature. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of a saturated solution of sodium thiosulfate. The mixture was extracted with methylene chloride (2 × 50 mL). The extracts were dried over anhydrous magnesium sulfate and the solvent was removed to yield a crude product which was taken up in hexane and filtered through a short column of silica gel. Removal of the solvent afforded *p*-chlorophenyl disulfide (1.4 g, 97%), mp 70.0 °C (lit.<sup>12</sup> mp 73 °C).

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**Registry No.** Iodotrimethylsilane, 16029-98-4; CH<sub>3</sub>SO<sub>2</sub>Cl, 124-63-0; CH<sub>3</sub>CH<sub>2</sub>SO<sub>2</sub>Cl, 594-44-5; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SO<sub>2</sub>Cl, 1939-99-7; C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl, 98-09-9; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, 98-59-9; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Br, 1950-69-2; *p*-BrC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, 98-58-8; *p*-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, 98-60-2; *p*-FC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, 349-88-2; *p*-FC<sub>6</sub>H<sub>4</sub>SOCl, 50986-83-9; *p*-FC<sub>6</sub>H<sub>4</sub>SCl, 1535-35-9; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Na, 824-79-3; *p*-FC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Me, 455-15-2; CH<sub>3</sub>SSCH<sub>3</sub>, 624-92-0; CH<sub>3</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>3</sub>, 110-81-6; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SSC<sub>6</sub>H<sub>5</sub>, 150-60-7; C<sub>6</sub>H<sub>5</sub>SSC<sub>6</sub>H<sub>5</sub>, 882-33-7; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SSC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*, 103-19-5; *p*-BrC<sub>6</sub>H<sub>4</sub>SSC<sub>6</sub>H<sub>4</sub>Br-*p*, 5335-84-2; *p*-ClC<sub>6</sub>H<sub>4</sub>SSC<sub>6</sub>H<sub>4</sub>Cl-*p*, 1142-19-4; *p*-FC<sub>6</sub>H<sub>4</sub>SSC<sub>6</sub>H<sub>4</sub>F-*p*, 405-31-2.

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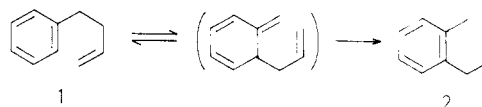
## Base-Assisted "Carbon-Claisen" Rearrangement of 4-Phenyl-1-butene

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The [3,3] sigmatropic rearrangements of all carbon systems in which one unsaturated site is constrained within an aromatic ring are poorly understood despite the fact that such rearrangements are related to both the Cope and Claisen rearrangements. No conversion of 4-phenyl-1-butene (1) to 3-(*o*-tolyl)propene (2) was observed in the



thermolysis of 1 in a flow system at 400 °C and above<sup>1</sup> or in sealed tubes at 400 °C.<sup>2</sup> Similarly, various 4-aryl-1-butenes, some embellished with substituents known to facilitate Cope rearrangements, gave upon thermolysis only traces of materials which could have arisen from [3,3] sigmatropic rearrangements.<sup>2,3</sup> In contrast, 1 has been reported to give a high yield of a mixture of *o*-tolylpropenes when heated at 350 °C in the presence of potassium *tert*-butoxide.<sup>4</sup> Thus, it was postulated that the first step in the conversion of 1 to 2, the sigmatropic rearrangement, was reversible and occurred readily at 350 °C, but the second step, isomerization of the intermediate to 2, was slow. The added base served as a catalyst for the second step.<sup>5</sup> Recently, however, elegant deuterium-labeling studies by Lambert, Fabricius, and Napoli have shown that the [3,3] sigmatropic rearrangement step for a 4-aryl-1-butene must be a high-energy process.<sup>9</sup> Taken together, these results suggest an unusual role for the base in the reported conversion of 1 to 2 and its isomers. With the intention of characterizing this base effect, we planned a <sup>13</sup>C isotope labeling study, but we have found, contrary to the previous report, that 1 is not converted to *o*-tolylpropenes upon thermolysis in the presence of potassium *tert*-butoxide.

Eight C<sub>10</sub>H<sub>12</sub> isomers (five phenylbutenes and three *o*-tolylpropenes) might be detected in the reaction mixtures after thermolysis of 1 in the presence of potassium *tert*-butoxide. We were able to resolve all eight isomers by gas chromatography on an XF-1150 column and, thus, could analyze products directly. Compound 2 was not completely resolved from (*E*)-1-phenyl-2-butene and (*Z*)-1-phenyl-1-butene and could not have been detected by our technique if present in small amounts (<5%). However, the predominant *o*-tolylpropene present after a base-catalyzed equilibration of 2 is (*E*)-1-(*o*-tolyl)propene which was

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(2) Lambert, J. B.; Fabricius, D. M.; Hoard, J. A. *J. Org. Chem.* **1979**, *44*, 1480-1485.

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