

Reduction of Arylsulfonyl Derivatives with the Sm/Cp₂TiCl₂ System. A Novel Method for Preparation of Disulfides[†]

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You Huang,^a Hongyun Guo,^b Yongmin Zhang^{*a} and Yulu Wang^c

^aDepartment of Chemistry, Zhejiang University at Xixi Campus, Hangzhou, 310028, P.R. China.

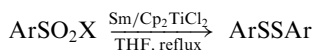
^bDepartment of Chemistry, Zhejiang Normal University, Jinhua, 321004, P.R. China.

^cDepartment of Chemistry, Henan Normal University, Xinxiang, 453002, P.R. China.

The Sm/Cp₂TiCl₂ system reduces arylsulfonyl derivatives to the corresponding disulfides in good yield in refluxing THF.

Disulfides are available as starting materials, and are useful as a class of synthetic intermediates in organic synthesis.^{1–4} Sulfonyl chlorides can be easily and efficiently prepared by chlorosulfonation reactions of arenes and alkanes.⁵ Therefore, the reduction of sulfonyl chlorides to disulfides is an important process in organic synthesis. As a result many reagents for this purpose have been reported, such as piperdinium tetrathiotungstate,⁶ sodium cyanoborohydride,⁷ iodotrimethylsilane,⁸ aluminium iodide,⁹ boron triiodide,¹⁰ and diphosphorus tetraiodide.¹¹

Recently, samarium reagents have been widely applied to organic synthesis,¹² at the same time, many reports in which Cp₂TiCl₂ is used as a catalyst in organic synthesis have been published.^{13,14} In our previous work, the Sm/Cp₂TiCl₂ system, which our group has established, is a very effective reducing system.^{15,16} In order to investigate the properties of this system and extend the scope of usage further, we thought that samarium and a catalytic amount of Cp₂TiCl₂ might be also a very effective reducing system. Here we report a new procedure for reduction of arylsulfonyl derivatives to the corresponding disulfides with samarium and catalytic amount of Cp₂TiCl₂ (Scheme 1).

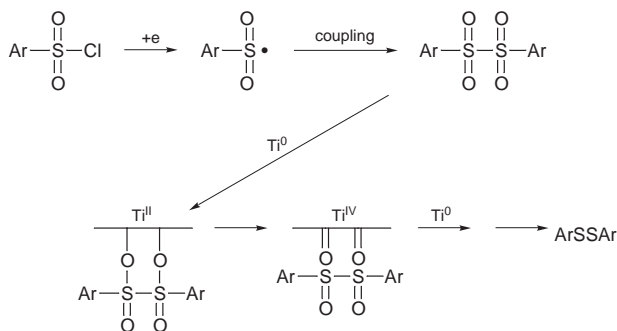
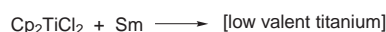


Scheme 1 X = Cl, Br, Na⁺

To establish the optimum reaction conditions, reduction of *p*-tolylsulfonyl chloride with metallic samarium and various amounts of Cp₂TiCl₂ was examined in THF under a nitrogen atmosphere. Table 1 shows that samarium (2 mmol) with Cp₂TiCl₂ (0.8 mmol) under refluxing THF is the best combination for reduction of *p*-tolylsulfonyl chloride to the corresponding disulfide (entry 5). The reaction also worked well when various amounts of Cp₂TiCl₂ and samarium in refluxing THF (entries 4–7) were used. No reaction occurs with only samarium or Cp₂TiCl₂ (entries 1 and 2) and no reaction takes place with samarium and Cp₂TiCl₂ and room temperature in THF (entry 3).

As shown in Table 2, this system not only can reduce arylsulfonyl chlorides but also can reduce arylsulfonyl bromide (entry 9) and sodium arylsulfinate (entries 10 and 11) efficiently. The reduction of arylsulfonyl chlorides containing electronic donating (entry 6) or electronic withdrawing groups (entries 4, 5, 7 and 12) indicate that the electronic environment of aryl group does not influence the reduction. The high yields of the reduction products demonstrate the efficiency of this new method.

Although the mechanism of the reduction process is not clearly defined a possible mechanism is shown in Scheme 2.



Scheme 2

Table 1 Reduction of *p*-tolylsulfonyl chloride (1 mmol) with metallic samarium and various amounts of Cp₂TiCl₂

Entry	Sm (mmol)	Cp ₂ TiCl ₂ (mmol)	Reaction conditions	Yield ^a (%)
1	2	0	Reflux 5 h	0
2	0	2	Reflux 5 h	0
3	2	4	r.t. 5 h	0
4	2	4	Reflux 30 min, r.t. 10 min.	41
5	2	0.8	Reflux 5 h	86
6	2	0.2	Reflux 5 h	60
7	2	0.1	Reflux 5 h	51

^a Yield refers to isolated yield of di(*p*-tolyl) sulfide.

Table 2 Reduction of sulfonyl derivatives to disulfides with Sm/Cp₂TiCl₂^a

Entry	RSO ₂ X	mp/°C (lit.)	Isolated yield (%)
1	4-MeC ₆ H ₄ SO ₂ Cl	43–44/44–46 ¹⁷	86
2	2-MeC ₆ H ₄ SO ₂ Cl	36–38/38–39 ^{18a}	76
3	C ₆ H ₅ SO ₂ Cl	58–59/58–60 ¹⁷	83
4	4-BrC ₆ H ₄ SO ₂ Cl	91–92/93.5 ⁷	80
5	4-ClC ₆ H ₄ SO ₂ Cl	68–69/69–71 ¹⁷	84
6	4-MeOC ₆ H ₄ SO ₂ Cl	40–42/41–43 ¹⁷	72
7	4-Cl,3-MeC ₆ H ₃ SO ₂ Cl	48/48–50 ¹⁹	84
8	2,4,6-Me ₃ C ₆ H ₂ SO ₂ Cl	121–123/123–125 ¹⁷	79
9	4-MeC ₆ H ₄ SO ₂ Br	44/44–46 ¹⁷	81
10	C ₆ H ₅ SO ₂ Na	59/58–60 ¹⁷	73
11	4-MeC ₆ H ₄ SO ₂ Na	43–45/44–46 ¹⁷	77
12		130/131–132 ^{18b}	76

^a All products gave satisfactory IR and ¹H NMR spectra. Reaction conditions: reflux for 5 h.

*To receive any correspondence.

[†]This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Current available methods have some disadvantages. For example, when sodium cyanoborohydride⁷ is used in the reduction of arylsulfonyl chlorides, although good chemoselectivity is observed, the reagents used are relatively expensive and toxic. Iodotrimethylsilane⁸ similarly is very expensive. Piperdinium tetrathiotungstate⁶ can be used under mild conditions, but it is difficult to prepare. The Sm/Cp₂TiCl₂ system thus offers an attractive alternative to the methods for preparation of disulfides. Its advantages are satisfactory yield, easily available starting materials, simple operation and neutral conditions.

Experimental

A typical procedure for reduction of sulfonyl derivatives is as follows: under a nitrogen atmosphere, 0.30 g (2 mmol) of Sm and 0.20 g (0.8 mmol) of Cp₂TiCl₂ were mixed in 10 ml of THF in a three-necked flask. After stirring under reflux for 15 min, a deep blue solution was obtained. Sulfonyl chloride (1 mmol) in THF (3 ml) was added, the solution turned red at once and the reaction was continued for 5 hours (monitored by TLC), before cooling to room temperature. The solution was then evaporated under reduced pressure, 50 ml of ether and 5 ml of 1 M HCl were added and the solution filtered, the organic layer was then dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the residue was purified by preparative TLC on silica gel (petroleum ether as eluent). Results are summarized in Table 2.

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