J. Chem. Research (S),
1999, 214–215†

Reduction of Arylsulfonyl Derivatives with the Sm/Cp_2TiCl_2 System. A Novel Method for Preparation of Disulfides†

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The Sm/Cp_2TiCl_2 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 Cp_2TiCl_2 is used as a catalyst in organic synthesis have been published.[13,14] In our previous work, the Sm/Cp_2TiCl_2 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 Cp_2TiCl_2 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 Cp_2TiCl_2 (Scheme 1).

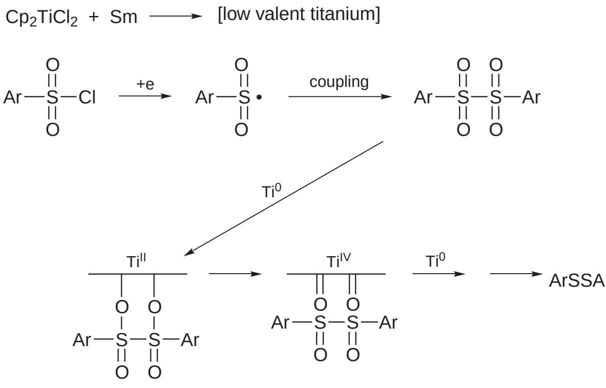
$$ArSO_2X \xrightarrow[\text{THF, reflux}]{Sm/Cp_2TiCl_2} ArSSAr$$

Scheme 1 $X = Cl, Br, Na^+$

To establish the optimum reaction conditions, reduction of *p*-tolylsulfonyl chloride with metallic samarium and various amounts of Cp_2TiCl_2 was examined in THF under a nitrogen atmosphere. Table 1 shows that samarium (2 mmol) with Cp_2TiCl_2 (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 Cp_2TiCl_2 and samarium in refluxing THF (entries 4–7) were used. No reaction occurs with only samarium or Cp_2TiCl_2 (entries 1 and 2) and no reaction takes place with samarium and Cp_2TiCl_2 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 arysulfonyl 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.



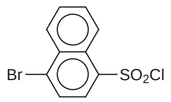
Scheme 2

Table 1 Reduction of *p*-tolylsulfonyl chloride (1 mmol) with metallic samarium and various amounts of Cp_2TiCl_2

Entry	Sm(mmol)	Cp_2TiCl_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/Cp_2TiCl_2[a]

Entry	RSO_2X	mp/°C (lit.)	Isolated yield (%)
1	$4\text{-}MeC_6H_4SO_2Cl$	43–44/44–46[17]	86
2	$2\text{-}MeC_6H_4SO_2Cl$	36–38/38–39[18a]	76
3	$C_6H_5SO_2Cl$	58–59/58–60[17]	83
4	$4\text{-}BrC_6H_4SO_2Cl$	91–92/93.5[7]	80
5	$4\text{-}ClC_6H_4SO_2Cl$	68–69/69–71[17]	84
6	$4\text{-}MeOC_6H_4SO_2Cl$	40–42/41–43[17]	72
7	$4\text{-}Cl,3\text{-}MeC_6H_3SO_2Cl$	48/48–50[19]	84
8	$2,4,6\text{-}Me_3C_6H_2SO_2Cl$	121–123/123–125[17]	79
9	$4\text{-}MeC_6H_4SO_2Br$	44/44–46[17]	81
10	$C_6H_5SO_2Na$	59/58–60[17]	73
11	$4\text{-}MeC_6H_4SO_2Na$	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.

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†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 cyanoborohydride[7] is used in the reduction of arylsulfonyl chlorides, although good chemoselectivity is observed, the reagents used are relatively expensive and toxic. Iodotrimethylsilane[8] similarly is very expensive. Piperdinium tetrathiotungstate[6] can be used under mild conditions, but it is difficult to prepare. The Sm/Cp_2TiCl_2 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 Cp_2TiCl_2 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.

We thank the National Natural Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for financial support.

Received, 9th September 1998; Accepted, 30th November 1998
Paper E/8/05339A

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