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NOVEL REDUCTION OF ARYLSULFONYL CHLORIDES TO DISULFIDES WITH Sm/$NiCl_2$/KI SYSTEM

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Abstract: Arylsulfonyl chlorides can be readily reduced to corresponding disulfides with Sm/$NiCl_2$/KI system in moderate to good yields at 60°C.

Since arylsulfonyl chlorides are easily prepared by the chlorosulfonation of aromatic compounds with chlorosulfonic acid[1], their conversion to other organic sulfur compounds with sulfur in the lower oxidation states is synthetically useful. Among these, organic disulfides are a class of useful synthetic intermediates because of its use in a variety of chemical transformations[2,3]. Many reagents have been used to reduce the sulfonyl halides to the corresponding disulfides, such as sodium tellurated borohydride $NaBH_2Te_3$[4], piperidinium tetrathiotungstate ()$_2WS_4$[5], sodium cyanoborohydride $NaBH_3CN$[6], etc. Herein we wish to report a new method for the reduction of arylsulfonyl chlorides using Sm/$NiCl_2$/KI system, we found that arylsulfonyl

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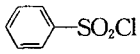
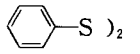
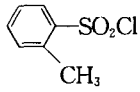
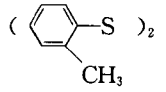
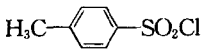
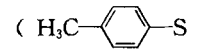
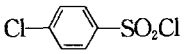
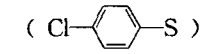
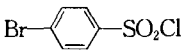
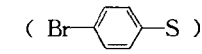
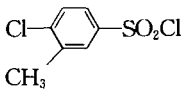
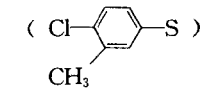
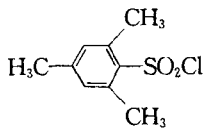
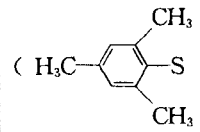
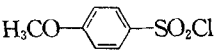
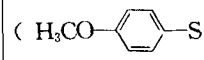
chlorides can be readily reduced to diaryldisulfides in moderate to good yields in HMPA at 60 ℃. Some results were summarized in the Table.

$$ArSO_2Cl \xrightarrow[60℃,\ 3h]{Sm/NiCl_2/KI} ArSSAr$$

Table Reduction of arylsulfonyl chlorides to disulfides with $Sm/NiCl_2/KI$ system

Entry	Substrate	Product*	Yield** %	m. p. ℃ (lit)[7]
1			70	58—60(61)[a]
2			60	35—37(38)[b]
3			62	43—45(46)[c]
4			74	68—70(71)[d]
5			68	89—91(93.5)[e]
6			74	50—52(48—50)[8]
7			68	122—125(125)[f]
8			63	41—43(44)[g]

* All products gave satisfactory IR and ^1H-NMR spectra

** Isolated yields

In view of the easily available starting materials, the chemoselectivity, good yield, neutral condition as well as the simple operation, we think that the present procedrue provides a useful method for the conversion of arylsulfonyl chlorides to disulfides.

Experimental Section

Melting points were uncorrected. HMPA was dried by CaH_2 and was then distilled in vacuo. ^1H NMR spectra were recorded with a PMX-60 spectrometer, using TMS as internal standard. IR spectra were determined on PE—683 spectrometer. Benzenesulfonyl, 2-toluenesulfonyl and 4-toluenesulfonyl chlorides are commercially available, other sulfonyl chlorides were prepared according to literature[1,8].

General procedure

Under an inert atmosphere of nitrogen, to a mixture of samarium (2 mmol), $NiCl_2$(0.8 mmol) and KI (4 mmol) was added a solution of arylsulfonyl chloride (1 mmol) in 4 ml HMPA. The slurry was stirred magnetically for 3 h at 60 ℃ and cooled to room temperature. 20 ml ether was added. organic layer was separated and aqueous layer was extracted with ether (2×20 ml). The combined organic layers were washed with water (30 ml × 3). After the solution was dried over anhydrous Na_2SO_4, the solution was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel (cyclohexane as eluent).

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