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
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NOVEL REDUCTION OF ARYLSULFONYL CHLORIDES TO DISULFIDES WITH Sm/NiCl₂/KI SYSTEM

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Abstract: Arylsulfonyl chlorides can be readily reduced to corresponding disulfides with Sm/NiCl₂/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 NaBH₂Te₃⁽⁴⁾, piperidinium tetrathiotungstate ( NH₂)₂WS₄⁽⁵⁾, sodium cyanoborohydride NaBH₃CN⁽⁶⁾, etc. Herein we wish to report a new method for the reduction of arylsulfonyl chlorides using Sm/NiCl₂/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 °C. Some results were summarized in the Table.

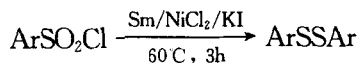
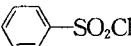
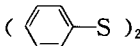
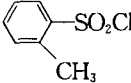
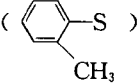
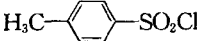
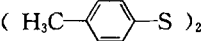
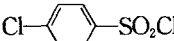

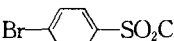

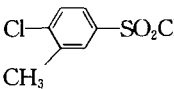
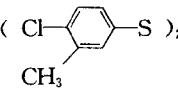
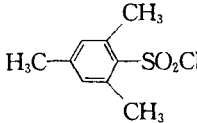
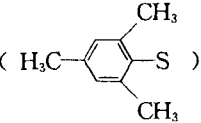
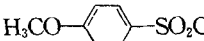
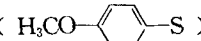


Table Reduction of arylsulfonyl chlorides to disulfides
with Sm/NiCl₂/KI system

Entry	Substrate	Product *	Yield * * %	m. p. °C (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 procedure 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°C 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 ($30\text{ ml} \times 3$). 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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