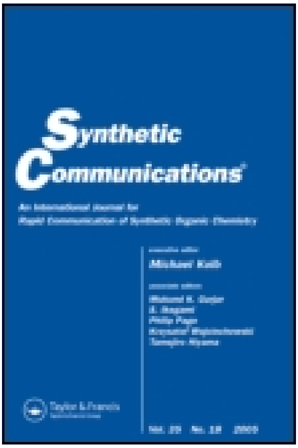

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The Reduction of Arylsulfonyl Chlorides and Sodium Arylsulfinates with $TiCl_4$/Sm System. A Novel Method for the Preparation of Diaryldisulfides

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THE REDUCTION OF ARYLSULFONYL CHLORIDES AND SODIUM ARYLSULFINATES WITH $TiCl_4$/Sm SYSTEM. A NOVEL METHOD FOR THE PREPARATION OF DIARYLDISULFIDES

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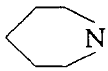
ABSTRACT: $TiCl_4$/Sm system reduces arylsulfonyl chlorides and sodium arylsulfinates to corresponding diaryldisulfides in moderate to good yields in THF at 60℃.

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]. As a result many reagents have been used for the reductive coupling of sulfonyl chlorides to the corresponding disulfides, such as sodium tellurated borohydride $NaBH_2Te_3$[4], piperidinium tetrathiotungstate ( $NH_2)_2WS_4$[5],

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sodium cyanoborohydride $NaBH_3CN$[6], aluminium triiodide AlI_3[7], boron triiodide BI_3[8],diphosphorus tetraiodide P_2I_4[9],etc.

Recently, low-valent titanium reagents[10] and samarium reagents[11] have been of great interest in organic synthesis respectively. We have recently reported the reductive deoxygenation of sulfoxides with $TiCl_4$/Sm system[12]. In the cause of exploring further the synthetic utility of $TiCl_4$/Sm system, we found that arylsulfonyl chlorides and sodium arylsulfinates can be readily reduced to diaryldisulfides in moderate to good yields in THF at 60℃(See scheme). Some results were summarized in the Table.

Experiment Section

The solvent tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to its use. ^{1}HNMR spectra were recorded on a JEOL JUM —PMX 60 SI (60MHz) instrument using TMS as internal standard. Melting points were uncorrected. Benzenesulfonyl and *p*-toluenesulfonyl chlorides are commercially available, other sulfonyl chlorides were prepared according to known literature[13]. Sodium arylsulfinates were dehydrated prior to reduction.

General procedure for the reduction of arylsulfonyl *chlorides and sodium arylsulfinates*:

Under an inert atmosphere of nitrogen, 1. 14g (6mmol) $TiCl_4$ was added by syringe to a stirred slurry of 0. 3g (2mmol) powdered samarium in 20 ml THF in a 50ml three—neck flask. The mixture was stirred magnetically for 1h at room temperature. A light blue suspension was obtained. A solution of arylsulfonyl chloride(1mmol) in THF or solid sodium arylsulfinate (1mmol) was then added to this stirred suspension in one portion. The mixture was stirred for 2h at 60℃ and cooled to room temperature. A dilute solution of HCl(5%,

Scheme

$$ArSO_2Cl \xrightarrow[60℃,2h]{TiCl_4/Sm/THF} ArSSAr$$

(a): Ar $=C_6H_5$- (d): Ar $=4$-BrC_6H_4-
(b): Ar $=4$-$CH_3C_6H_4$- (e): Ar $=3$-CH_3-4-ClC_6H_3-
(c): Ar $=4$-ClC_6H_4-

$$ArSO_2Na \xrightarrow[60℃,2h]{TiCl_4/Sm/THF} ArSSAr$$

(f): Ar $=C_6H_5$- (h): Ar $=4$-ClC_6H_4-
(g): Ar $=4$-$CH_3C_6H_4$-

Table. Physical and spectral data of the products

Entry	m. p/lit.[6](℃)	yield* (%)	$^1HNMR(CCl_4),\delta(ppm)$
a	55—56/60	65	7.0—7.68(m)
b	42.5—44/48	62	2.33(s,6H),6.9—7.48(m,8H)
c	68—70/72	74	7.07—7.50(m)
d	89—90/94	77	7.33—7.43(m)
e	48—50	61	2.33(s,6H),7.1—7.33(m,6H)
f	56—58/60	83	7.08—7.67(m)
g	42—44/48	80	2.29(s,6H),6.92—7.5(m,8H)
h	68—69/72	76	7.0—7.50(m)

* Yields of isolated products.

* * All products gave satisfactory IR spectra(S—S, ν=550—400cm^{-1}).

10ml) and ether (20ml) were added. The organic layer was seperated and the aqueous layer was extracted with ether (20ml). The combined organic solution was washed with water (20ml × 3) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel(cyclohexane as eluent).

In view of the easily available starting materials, satisfactory yield, simple experimental procedure and neutral conditions, the present procedure offers an attractive alternative to the methods for the preparation of diaryldisulfides.

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References

1. Suter, C. M., The Organic Chemistry of Sulfur; Intrascience Research Foundation: Santa Monica, CA, 1969.
2. Ogawa, A., Nishiyama, Y., Kambe, N., Murai, S. and Sonoda, N., Tetrahedron Lett., 1987,28,3271.
3. Antebi, S. and Alper, H., Tetrahedron Lett., 1985,26, 2609.
4. Suzuki, H., Nakamura, T. and Yoshikawa, M., J. Chem. Res. (S)., 1994,2,70
5. Dhar, P., Ranjan, R. and Chandrasekaran, S., J. Org. Chem., 1990, 55,3728.
6. Kagabu, S., Org. Prep. Proced. Int., 1989,21,388.
7. Babu, J. R., Bhatt, M. V. Tetrahedron Lett., 1986,27, 1073.
8. Olah, G. A., Narang, S. C., Field, L. D. and Karpeles, R., J. Org. Chem., 1981, 46,2408.
9. Suzuki, H., Tani, H. and Osuka, A., Chem. Lett., 1984, 1,139.
10. McMurry, J. E., Chem. Rev., 1989,89,1513.
11. Molander, G. A., Chem. Rev., 1992,92,29.
12. Wang, J. Q., Zhang, Y. M., Synth. Commun., in press.
13. Huntress, E. H., Carten, F. H., J. Am. Chem. Soc., 1940,62,511.

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