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Facile and Mild Reduction of Sulfoxides to Sulfides with $TiCl_4$/Sm System

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FACILE AND MILD REDUCTION OF SULFOXIDES TO SULFIDES WITH $TiCl_4$/Sm SYSTEM

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ABSTRACT: $TiCl_4$/Sm system reduces sulfoxides rapidly to the corresponding sulfides in good yields in THF at room temperature.

Reduction of sulfoxides to corresponding sulfides is a recurring theme in organic chemistry because of its use in various synthetic tranformations. As a result several methods have been developed for the reduction of sulfoxides[1,2,3,4]. We have also reported the reduction of sulfoxides with Cp_2TiCl_2/i-PrMgBr[5], $FeCl_3/NaBH_4$[6], SmI_2[7] and Cp_2TiCl_2/Sm[8]. Herein we wish to report a new efficient method for this conversion with $TiCl_4$/Sm reagent system.

In our experiment work, we found that sulfoxides can be rapidly reduced to the corresponding sulfides by $TiCl_4$/Sm system

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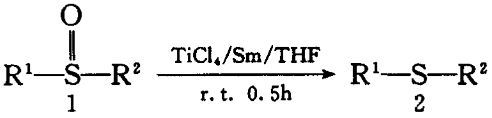
in good yields in THF at room temperature. The reaction can be envisaged to proceed in two stages. In the first, $TiCl_4$ is reduced by samarium metal to form a low—valent titanium species, which in the subsequent step would deoxygenate sulfoxide 1 to form sulfide 2. Some results were summarized in the Table.



$$\underset{1}{R^1-\overset{\overset{O}{\|}}{S}-R^2} \xrightarrow[\text{r.t. 0.5h}]{TiCl_4/Sm/THF} \underset{2}{R^1-S-R^2}$$

Experiment Section

The solvent tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to its use. NMR spectra were recorded on a PMX—60MHz instrument using T MS as internal standard.

General procedure for the reduction of sulfoxide:

Under an inert atmosphere of nitrogen, 0.76g (4mmol) $TiCl_4$was added by syringe to a stirred slurry of 0.3g(2mmol)

Table Reduction of Sulfoxides with $TiCl_4$/Sm system.

Product	R^1	R^2	yield* (%)
2a	Ph	Ph	75
2b	4—ClC_6H_4	4—ClC_6H_4	81
2c	Ph	$PhCH_2$	80
2d	$PhCH_2$	$PhCH_2$	78
2e	Ph	CH_3	87
2f	Ph	C_2H_5	84
2g	Ph	n—C_4H_9	84

*. Yields of isolated products.

* *. All Products were characterized by comparison of their IR and ^{1}HNMR with authentic samples.

powdered samarium in 15ml 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 sulfoxide (1mmol) in THF was then added by syringe to this stirred suspension. The mixture turned red—brown almost immediately and was stirred continually for 0. 5h at room temperature. A dilute solution of HCl and ether were added. The organic layer was washed with water(20ml×3)and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. The crude product was purified by preparative TLC on silica (cyclohexane as eluent).

The present procedure offers an attractive alternative to the methods for reduction of sulfoxides currently available with its mildness, convenience and rapidity as well as good yields.

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