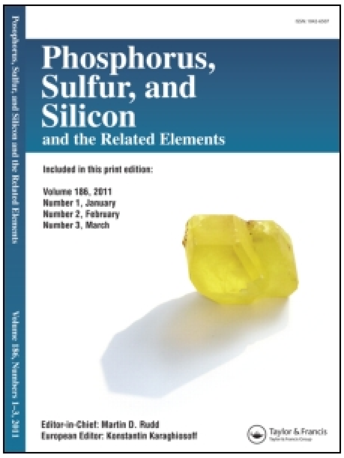

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A NEW EASY CONVERSION OF SULFOXIDES TO SULFIDES

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A NEW EASY CONVERSION OF SULFOXIDES TO SULFIDES

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This paper describes a new reaction for the conversion of sulfoxides to sulfides by boron trifluoride and sodium iodide, both readily available and low-cost reagents. Very short reaction times, easy work up and almost quantitative yields make this reaction interesting from a synthetic point of view.

Sulfoxides are well known to give coordination complexes with Lewis acids and have been reported[1] to react rather smoothly at room temperature with boron trihalides leading to stable complexes containing oxygen–boron bonds.[2]

The formation of such complexes could be exploited conveniently for enhancing reactivity of the electrophilic sulfur atom of sulfoxides toward nucleophilic reagents, thus prompting the use of easily removable nucleophiles to accomplish sulfur–oxygen bond cleavage and thereby conversion of sulfoxides to the corresponding sulfides under mild conditions.

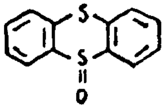
Toward this end, we have now devised a new method for sulfoxide deoxygenation utilizing boron trifluoride and sodium iodide. These reagents, under the experimental conditions which are reported below (sulfoxide : BF_3 : NaJ = 1 : 5 : 5 in anhydrous acetone), gave very satisfactory results which have been summarized in the Table.

As far as the mechanistic course of the reduction is concerned, one could assume confidently that the sulfoxide/BF_3 complex, which is formed in the early stages of the overall reaction, first undergoes nucleophilic attack at the sulfur atom by the iodide ion. Then, in a subsequent step, the species therefrom undergoes in its turn nucleophilic attack, by the excess iodide ion still present in the reaction mixture, at the iodine atom. This leads to molecular iodine formation and sulfur–oxygen bond cleavage with the loss of an oxygenated boron moiety of the molecule. Indeed, the pure BF_3 complex, specially prepared[1] from dimethyl sulfoxide, immediately underwent conversion to dimethyl sulfide when treated with sodium iodide under our experimental conditions. Furthermore, molecular iodine is formed in the reaction and in one experiment it was determined by titration and found to be in a 1 : 1 molar ratio with the starting sulfoxide. However, no evidence could be obtained as to the nature and fate of the boron-containing species which is lost during the reaction.

The 1 : 5 : 5 ratio of the reagents is quite empirical. Lower sulfoxide : BF_3 ratios slowed the reaction down (e.g. *Cf.* 1 : 2.5 : 5 ratio reported in the Table) and led at the same time to poorer yields, likely due to a possible competition[3] between acetone and sulfoxide in the complexation stage. Moist acetone led to poor results

TABLE

Conversion of sulfoxides to sulfides by BF_3/NaJ

	Sulfoxide : BF_3 : NaJ				Sulfides °C		Microanalyses[b]			
	1 : 5 : 5		1 : 2.5 : 5							
Sulfoxides	Time	% Yield[a]	Time	% Yield[a]	m.p. or b.p./torr	lit. data				
Me_2SO	5′	92	60′	80	38°/760	37.3°/760[7]		C, 39.08;	H, 9.67;	S, 51.25%
							calc.	38.70;	9.74;	51.56
Me—SO-ϕ	10′	91	60′	76	191°/760	80°/15[8]		C, 67.33;	H, 6.55;	S, 26.12%
							calc.	67.73;	6.50;	25.77
n-C_4H_9—SO-ϕ	10′	93	70′	80	102°/10	92–95°/4[8]		C, 72.53;	H, 8.41;	S, 19.06%
							calc.	72.26;	8.49;	19.25
n-C_4H_9—SO-ϕ—Me	10′	94	60′	86	120°/15	113°/13[8]		C, 73.42;	H, 8.98;	S, 17.60%
							calc.	73.30;	8.95;	17.75
Me_3C—SO-ϕ	90′	65	6h	52	80°/10	92–93°/14[9]		C, 72.01;	H, 8.53;	S, 19.46%
							calc.	72.26;	8.49;	19.25
ϕ-CH_2—SO-ϕ	15′	93	60′	82	38–41°	40°[8]		C, 77.65;	H, 5.98;	S, 16.37%
							calc.	77.98;	6.04;	15.98
(ϕ-CH_2)$_2$SO	15′	94	60′	85	48–49°	49–50°[7]		C, 78.70;	H, 6.52;	S, 14.78%
							calc.	78.48;	6.59;	14.93
(ϕ-CH_2)$_2$SO (−40°C)	120′	90								
	10′	98	50′	88	156–157°	155–156°[10]		C, 66.48;	H, 3.76;	S, 29.76%
							calc.	66.67;	3.73;	29.60.

[a] Yield of pure isolated product; purity > 94% (as determined by H-NMR and GLC analysis).
[b] The analyses were performed by Mikroanalytisches Laboratorium E. Thommen, Bettingen (Switzerland).

likely owing to the formation of BF_3 hydrates[4] which are known to be rather stable. Use of other solvents, for example either dichloromethane or diethyl ether (it is worth noting that preparation of sulfoxide/BF_3 complexes is carried out only in this solvent), again led to unsatisfactory results which conveniently can be accounted for by a diminished[5] nucleophilic reactivity of iodide ions in these solvents.

The chemistry of sulfoxides is a subject of current interest[6] and numerous reagents are known already for the conversion of sulfoxides to sulfides. In our opinion the present procedure may have the advantage of being quite general for aliphatic, aromatic and mixed sulfoxides, utilizing easily available and low-cost reagents, giving very fast, quite clean and almost quantitative reductions, even at rather low temperatures (−40°C).

EXPERIMENTAL

Preparation of Dibenzyl Sulfide—General Procedure.

To a magnetically-stirred solution of dibenzyl sulfoxide (1.0 g, 4.3 mmol) and sodium iodide (3.2 g, 21.7 mmol) in anhydrous acetone (30 ml) cooled in an ice bath, freshly distilled boron trifluoride etherate (2.7 ml, 21.7 mmol) was added dropwise. The clear solution turned immediately to a deep red color with the formation of a precipitate. Within 10 min the reaction was complete (TLC monitoring) and the brown suspension was poured into water (150 ml) and extracted with Et_2O (3 × 100 ml). The combined ethereal layers then were washed with 5 N aq. sodium thiosulfate (50 ml) and water (50 ml), dried over sodium sulfate and evaporated. The residual crystalline product after recrystallization from hexane gave pure dibenzyl sulfide, yield: 0.87 g (94%); m.p. 48–49°C (lit[7] 49–50°C).

The same reaction, when carried out at −40°C, was complete in 2 hours and afforded dibenzyl sulfide in 90% yield after recrystallization.

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