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NEW REAGENTS 4[1]. REDUCTION OF SULPHONYL CHLORIDES AND SULPHOXIDES WITH ALUMINIUM IODIDE

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ABSTRACT: Aluminium iodide reduces sulphonyl chlorides to disulphides and sulphoxides to sulphides under mild conditions in acetonitrile.

While exploring the synthetic applications of the strong Lewis acid property of aluminium iodide, we found that it behaves also as a reducing agent. We wish to report that aryl and alkyl sulphonyl chlorides are converted into disulphides in excellent yields under mild conditions in acetonitrile medium (See Table 1).

Reduction of equimolar mixture of p-toluenesulphonyl chloride and p-bromobenzenesulphonyl chloride gave a mixture of disulphides viz., bis-(4-bromophenyl)disulphide, 4-bromophenyl 4-methylphenyl disulphide and bis-(4-methylphenyl)disulphide in the ratio of 1:2:1. Same mixture was also obtained by the reduction of 4-bromophenyl 4-methylphenyl disulphone indicating that some radical intermediates are involved. Our studies on the mechanism of this reaction do not yet enable us to define a unique mechanism.

We have also found that aryl and alkyl sulphoxides are reduced to sulphides by aluminium iodide (See Table 2).

A number of reagents have been reported to reduce sulphonyl chlorides to disulphides.[2] A recent review summarises the reagents used for the reduction and sulphoxides to sulphides.[3] From the point of view of easy accessibility and mild conditions needed for reduction, aluminium iodide seems to be a quite attractive reducing agent.

Table I: Reduction of sulphonyl chlorides to disulphides in acetonitrile.

RSO_2Cl	Mole proportion AlI_3 : Substrate	Reaction conditions	Yield (%)[5] of R-S-S-R
$4\text{-}CH_3\text{-}C_6H_4\text{-}$	1:1	4 hr. r. t.	82
$4\text{-}CH_3\text{-}C_6H_4\text{-}$	1:1	3 hr. r. t. 1 hr. reflux	90
$4\text{-}Br\text{-}C_6H_4\text{-}$	1.4:1	5 hr. r. t. 1 hr. reflux	93
$2\text{-}C_{10}H_7\text{-}$	1.4:1	4 hr. r. t. 1 hr. reflux	95
$C_6H_5\text{-}$	1.4:1	4 hr. r. t. 1 hr. reflux	94.5
$C_6H_5CH_2\text{-}$	1.4:1	4 hr. r. t. 45 min. reflux	82
$n\text{-}C_4H_9\text{-}$	1.4:1	4 hr. r. t. 30 min. reflux	81

In a typical procedure p-bromobenzenesulphonyl chloride (511 mg, 2 mmol) in 2 ml CH_3CN) was added to a freshly prepared solution of AlI_3[1] (2.8 mmol) in CH_3CN (6 ml) and stirred at room temperature for five hours and further refluxed for one hour. The reaction mixture was worked up as usual[1] and the crude product was purified using a column of silica gel (eluent: petroleum ether b. p. 60°-80°C). Yield of bis-(4-bromophenyl)disulphide 350 mg (93 %); m.p. 95°C (Lit.[4] m.p. 94.5°C).

Table II: Reduction of sulphoxides to sulphides in acetonitrile.[6]

R-$\overset{O}{S}$-R.	Mole proportion AlI_3 : Substrate	Reaction conditions	Yield (%)[5] of R-S-R.
$n\text{-}C_4H_9$-	2:1	1 hr. r. t.	68
$C_6H_5CH_2$-	2:1	6 hr. reflux	84
C_6H_5-	2:1	55 hr. reflux	80[a]

[a] About 7 % of the starting material was recovered.

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References and Notes:

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2. H. Suzuki, H. Tani, A. Osuka, Chem. Lett. 139 (1984) and references cited therein.
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5. All the yields were based on isolated materials. The products were identified by physical constants and spectroscopic methods.
6. The procedure for the reduction of sulphoxides was essentially same as that for the reduction of sulphonyl chlorides except for the molar proportion of AlI_3 and the time of the reaction as indicated in Table 2.

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