Oxidation of Sulphides to Sulphoxides with 1-Chlorobenzotriazole

By WILLIAM D. KINGSBURY and CARL R. JOHNSON*

(*Department of Chemistry, Wayne State University, Detroit, Michigan* 48202)

Summary Sulphides are quickly and efficiently converted into sulphoxides, without concomitant formation of sulphones, by 1-chlorobenzotriazole.

REES and STORR[1] have reported the preparation of 1-chlorobenzotriazole and its ability to oxidize alcohols and hydrazo-compounds. In view of past successes in the oxidation of sulphides to sulphoxides by the use of positive halogen compounds[2] we examined the utility of this new reagent in such reactions. Our results are summarized in the Table. The method offers worthwhile advantages. The reagent is inexpensively, easily, and quickly prepared and has a long shelf-life. The reaction is fast, clean, goes in high yields, and over-oxidation to sulphone is not observed.

In a typical reaction, the 1-chlorobenzotriazole (2 mmole) dissolved in a small amount of methanol (*do not warm to effect solution*) was added dropwise to a solution of the sulphide (2 mmole) in methanol (10—25 ml.) cooled in a Dry Ice bath. After stirring for 10—45 min. at −78°, the reaction mixture was poured into an excess of 3% aqueous sodium hydroxide and mixed well. The benzotriazole by-product is soluble in the aqueous base. The sulphoxide was isolated by extraction with methylene chloride, after saturation of the aqueous phase with sodium chloride, if necessary, for efficient partition.

Such oxidation reactions could also be achieved under similar conditions using methylene chloride as solvent. In most cases, however, the reactions were not as clean. When dibenzyl sulphide in methylene chloride was subjected to the reagent at room temperature, benzyl chloride, dibenzyl disulphide, and other (unidentified) products were produced. In our hands, neither 1-chlorobenzotriazole nor t-butyl hypochlorite are successful for the conversion of di-t-butyl sulphide into its sulphoxide, possibly because of heterolysis of a sulphur–carbon bond at a reaction intermediate stage.

TABLE

Sulphide	Solvent	Sulphoxide (% isolated yield)
Thietan	MeOH	90
	CH_2Cl_2	90
Thiolan	MeOH	70
	CH_2Cl_2	68
Thian	MeOH	98
	CH_2Cl_2	95
Di-isopropyl sulphide ..	MeOH	87
Di-t-butyl sulphide ..	MeOH	0
	CH_2Cl_2	0
Methyl phenyl sulphide ..	MeOH	92
	CH_2Cl_2	92
4-Methylthioacetanilide ..	MeOH	84

When the reaction was carried out in the typical manner using methyl phenyl sulphide in methanol, but with 2 equiv. of oxidant, the only product obtained was methyl phenyl sulphoxide. However, when methyl phenyl sulphoxide in methanol was allowed to react at −78° with 1-chlorobenzotriazole, methyl phenyl sulphone was produced in 97% yield. Apparently the nature of this reaction is much like that of t-butyl hypochlorite and sulphides.[2]

This work was supported by the National Science Foundation.

(*Received, February 21st,* 1969; *Com.* 243.)

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[1] C. W. Rees and R. C. Storr, *Chem. Comm.*, 1968, 1305.

[2] For examples, see L. Skattebol, B. Boulette, and S. Solomon, *J. Org. Chem.*, 1967, **32**, 3111; R. Harville and S. P. Reed, *ibid.*, 1968, **33** 3976; C. R. Johnson and D. McCants, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 1109; and references cited therein.