A Simple Method for Converting Oxirans into Thiirans Stereospecifically

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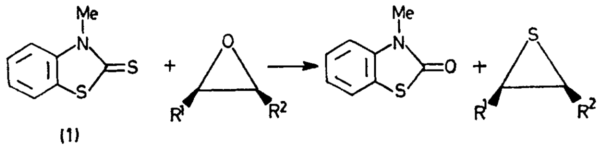
Summary 3-Methylbenzothiazole-2-thione in the presence of trifluoroacetic acid converts oxirans into thiirans stereospecifically.



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We report that thiirans may be synthesized rapidly and in almost quantitative yield from the corresponding oxirans by

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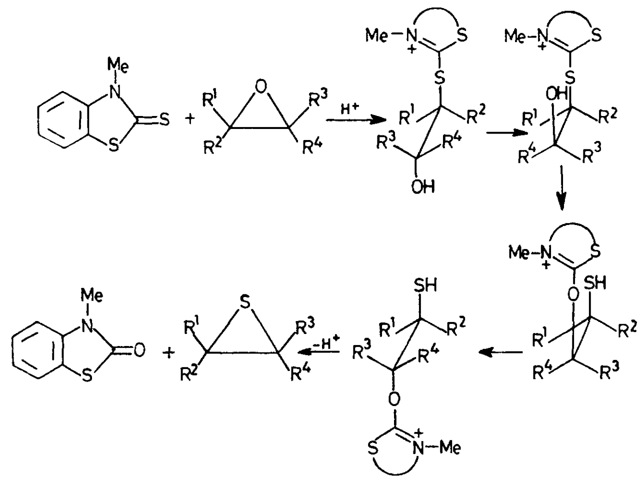
† L. Marchese, Thesis University of Bari, 1975—1976.

reaction with 3-methylbenzothiazole-2-thione[1] (**1**) and trifluoroacetic acid [reaction (1)].



SCHEME

CF_3CO_2H (0·55 mol) was added to a solution of (**1**) and the oxiran (0·55 mol each) in dry CH_2Cl_2 at 0 °C. After 5—10 min work up afforded the pure thiiran. Cyclohexene oxide, styrene oxide, epichlorohydrin, and *cis*-stilbene oxide all gave a quantitative yield of the corresponding thiiran; *trans*-stilbene oxide gave only 80% of the thiiran, probably owing to decomposition (*cf.* ref. 2). Products were identified by comparison with authentic samples synthesized by known procedures. Yields were determined after isolation of the thiirans by preparative t.l.c. or g.l.c.

The utility of this reaction was indicated by the conversion of styrene and stilbene oxides into the corresponding thiirans. Conventional methods using thiourea were unsuccessful.[3] Moreover the high yields, the simple synthesis[4] of the reagent (**1**), and the simplicity of the reaction make this method competitive with or better than the more recent method of thiiran synthesis.[5]

By analogy with the thiocyanate and thiourea reactions,[3] we propose the mechanism in the Scheme. In support of this mechanism, it was found that *cis*-stilbene oxide was converted exclusively into *cis*-stilbene sulphide.

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[1] For the nucleophilic properties of Δ^4-thiazolin-2-thione see: G. Roussell, R. Gallo, M. Chanon, and J. Metzger, *J.C.S. Perkin II*, 1974, 1304 and references therein; Y. Gelernt and P. Sykes, *J.C.S. Perkin I*, 1974, 2610.

[2] R. Ketcham and V. P. Shah, *J. Org. Chem.*, 1963, **28**, 229.

[3] M. Sander, *Chem. Rev.*, 1966, **66**, 297.

[4] H. W. Wanzlick, H. J. Kleiner, I. Lasch, H. U. Fuldner, and H. Steinmans, *Annalen*, 1967, **708**, 155.

[5] T. H. Chan and J. R. Finkenbine, *J. Amer. Chem. Soc.*, 1972, **94**, 2880.