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THE FIRST EXAMPLE OF A METAL-SUBSTITUTED THIIRANES TRIPHENYLSILYLTHIIRANE

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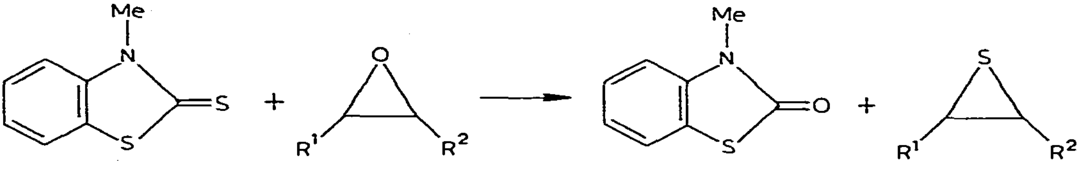
Summary

The first preparation of a metal substituted thiirane is described. 3-Methylbenzothiazole-2-thione (I) in the presence of trifluoroacetic acid converts triphenylsilyloxirane into the corresponding thiirane.

Introduction

It was recently [1] reported that thiiranes may be synthesized rapidly and in almost quantitative yield from the corresponding oxiranes by reaction with 3-methylbenzothiazole-2-thione (I) * and trifluoroacetic acid.



(I) (II) (III) (IV)

According to the authors [1] this method is competitive with (if no better than) the more recent method of thiirane synthesis [3]. For some time now we have been investigating the chemical properties, stereochemical stability and spectroscopic behaviour of organometal-derivatives containing small oxirane type rings [4,5] and we are examining the possibility of oxirane to thiirane ring transformation, brought about by conventional reagents such as thiourea and potassium sulphocyanide [6]. When the great efficiency of the reagent I compared with thiourea and potassium sulphocyanide became apparent we tried it out on our systems and found that, when triphenylsilyloxirane [7] (V) reacts with 3-methyl-

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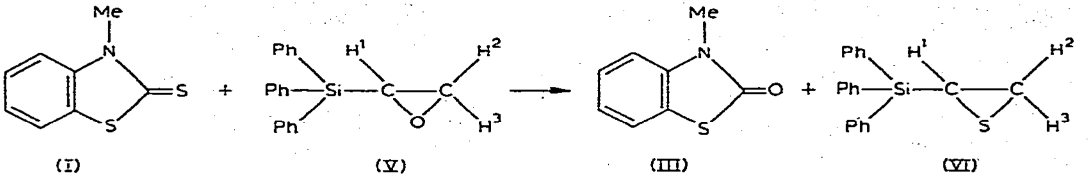
* For the synthesis of I see ref. 2.

benzothiazole-2-thione (I) under the conditions described by Calo' et al. [1], the analogous cyclic compound containing sulphur (triphenylsilylthiirane) VI is obtained in a yield of 53%.



The product has a m.p. of 120—121°C. The elementary analysis and the N.M.R. properties are in agreement with the proposed structure VI.

Experimental

Triphenylsilyloxirane (561.1 mg., 1.85 mmol.) and 3-methylbenzothiazole-2-thione (335 mg., 1.85 mmol.) were dissolved in anhydrous methylene chloride, and the mixture was cooled to 0°C. Trifluoroacetic acid (211 mg., 1.85 mmol.) was added and the clear colourless solution stirred for ten minutes. The solution was then added to 10 ml. of water and the mixture was cautiously neutralized with a saturated potassium carbonate solution and extracted with chloroform. After drying over potassium carbonate and evaporation of the solvent under vacuum below 40°C, a clear yellow oil was obtained. This was transferred to a chromatographic Florisil column and eluted with anhydrous pentane. Triphenylsilylthiirane was obtained as translucent crystals (yield 53%) m.p. 120—121°C.

Triphenylsilylthiirane: Found: C, 75.60; H, 5.86; S, 9.81. $C_{20}H_{18}SSi$ calcd.: C, 75.50; H, 5.70; S, 10.05%. ^{1}H NMR spectrum at 60 MHz with a JEOL-JNM C-60 HL spectrometer in chloroform-d_1 solution; δ H(1) 2.54 ppm; δ H(2) 2.096 ppm; δ H(3) 2.781 ppm; J(1—2) 6.34; J(1—3) 7.37; J(2—3) ~ 0.

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