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SYNTHESIS OF BRUGIEROL AND ISOBRUGIEROL, TRANS- AND CIS-4-HYDROXY-1,2-DITHIOLANE-1-OXIDE

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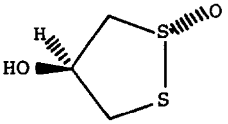
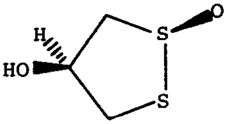
In a previous paper,[1)] brugierol and isobrugierol isolated from *Brugiera conjugata* (Rhizophoraceae) have been proposed to have structures as I and II, respectively, mainly on the basis of spectroscopic evidence. The present paper deals with the synthesis of I and II.

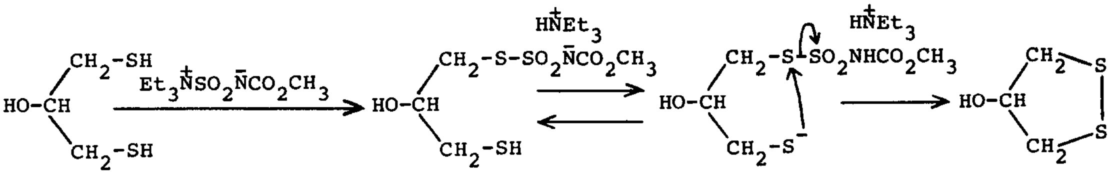


I



II

Recently, methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt (III) has been reported to be a novel reagent, which is useful for dehydrating *sec*- and *tert*-alcohols.[2)] It was expected, therefore, that this reagent might be applicable to the synthesis of 1,2-dithiolanes as shown in the following equation.[3)]



IV

To a solution of freshly distilled 2-hydroxy-1,3-dimercaptopropane[4)] (1.24 g) in chloroform was added a solution of III (2.50 g) in chloroform over a period of 15 min. under ice-cooling under a nitrogen atomosphere. After 15 min., the mixture was washed with a small amount of water and 0.5$\underline{\underline{N}}$ aq. sodium hydroxide and dried over magnesium sulfate to afford a golden yellow solution of 4-hydroxy-1,2-dithiolane (IV): UV $\lambda_{max}^{CHCl_3}$ 347 nm.5)

The resulting chloroform solution of IV was oxidized with 30% hydrogen peroxide (1.32 g) in chloroform-acetonitrile at room temperature for 48 hr. and evaporated under reduced pressure at room temperature to give an oily residue which was chromatographed on a silica gel column with chloroform-acetone (3:1). The first fraction, which showed a spot at Rf 0.30 on TLC,6) gave I (345 mg), mp 84-85° (from ethylacetate), and the second fraction, which showed a spot at Rf 0.24 on TLC,6) gave II (82 mg), as a colorless liquid. The compounds I and II synthesized were identified by elementary analyses and their IR, NMR and UV spectra, as well as by the direct comparison with natural products.1)

References

1) A. Kato and M. Numata, Tetrahedron Letters, 203 (1972).

2) E. M. Burgess, H. R. Penton, Jr. and E. A. Taylor, J. Am. Chem. Soc., **92**, 5224 (1970).

3) Similar equation has been proposed for the reaction of 1,4-dimercaptobutane with p-toluenesulfonyl chloride in aq. sodium hydroxide.7)

4) E. P. Adams, F. P. Doyle, D. L. Hatt, D. O. Holland, W. H. Hunter, K. R. L. Mansford, J. H. C. Nayler and A. Queen, J. Chem. Soc., 2649 (1960).

5) The UV spectrum of IV reported by Schmidt is very different from that of IV obtained in the present case, which is in good agreement with that of 1,2-dithiolanes.8) Attempts to isolate IV were unsuccessful because complete removal of solvent caused polymerization of the dithiolane.

6) Silica gel with chloroform-acetone (3:1). Two percents of palladium chloride in 2$\underline{\underline{N}}$ hydrochloric acid and a UV lamp (2536Å) were employed for the detection.

7) L. Field and R. B. Barbee, J. Org. Chem., **34**, 36 (1969).

8) von U. Schmidt, P. Grafen and H. W. Goedde, Ann., **670**, 157 (1963).