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Contribution to the Chemistry of Sulfur, No. 104 [1]

SYNTHESIS OF PENTATHIEPIN AND BENZOPENTATHIEPIN

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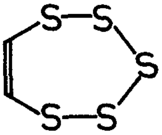
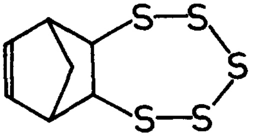
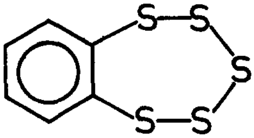
Recently we have synthesized several sulfur heterocycles with aliphathic carbon atoms as "hetero groups" by cyclic condensation of geminal or vicinal aliphathic dithiols with the corresponding chlorosulfanes, e. g. hexathiepane [2] as well as 1.2.3.4.-tetrathiadecalin and related systems [3]. Using similar procedures we have now prepared sulfur rings, which contain a C-C-double-bond.



(I)



(II)



(III)

Starting from cis-dimercaptoethylene [4] and dichlorotrisulfane [5], <u>pentathiepin</u> (I) can be prepared in good yield. 0.02 mole S_3Cl_2 and freshly prepared cis-dimercaptoethylene are dissolved each in 100 ml diethylether. (The unstable dithiol is prepared from the di-Na-salt with 6m HCl in aqueous solution and extracted with ether.) With stirring the solutions are added at an equal rate within 6 - 8 hours to 1.5 l dry ether under nitrogen atmosphere. The solution is stirred for several additional hours. After removing the solvent, an orange oil is obtained, which contains (I) in 80% yield. At low pressure and room temperature this oil may be purified by condensation in a trap cooled with acetone/ dry ice. Small amounts of the pure substance are obtained as yellow drops, which display a strong tendency to polymerisation. The purity is at least 95%.

Molecular weight by mass spectrometry 186; proton NMR spectrum: singlet at δ = 7.42 ppm (TMS). Characteristic absorptions in the IR spectrum (solutions of CCl_4 and CS_2): ν_{C-H} 3010 and 2970 cm^{-1}, $\nu_{C=C}$ 1630, δ_{C-H} 710, ν_{S-S} 485 and 470. UV spectrum in cyclohexane: the absorption curve shows weak shoulders at 315 nm (ε = 1510), 253 (3440), and 206 (9730).

To prepare the cyclopentadiene Diels-Alder adduct (II) of pentathiepin, a tenfold excess of cyclopentadiene is added to the originally obtained solution of (I) in ether. After several days the solution is concentrated and cooled. Colourless crystals are obtained, which are recrystallized from CCl_4; m.p. 121°, yield 30%. Elementary analysis, IR and the proton NMR spectrum support the assumed structure. Molecular weight by mass spectrometry 252; the UV spectrum shows maxima at 281 nm (ε = 3090) and 234 (5540).

For the synthesis of Benzopentathiepin [6] (III) from o-dimercaptobenzene [7] and S_3Cl_2 the reaction is completed as described for the preparation of (I). Then concentrating and cooling of the solution leads to crystallisation of (III), which is recrystallized from ether; yellow monoclinic crystals, m.p. 65-66°, yield 50%. The elementary analysis and the molecular weight of 236 are in accord with the assigned structure. NMR spectrum: AA'BB' system centered at δ = 7.52 ppm. Characteristic absorptions in the IR spectrum (KBr pill): ν_{Ar-S} 950, ν_{S-S} 480, 460 cm^{-1}. UV spectrum (cyclohexane): maximum at 213 nm (ε = 32500) and weak shoulders at 365 (1450), 308 (3950), 268 (5150), and 228 (21000).

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