REACTION OF 2,2'-DICYCLOHEXANONYL SULFIDE WITH HYDROGEN SULFIDE

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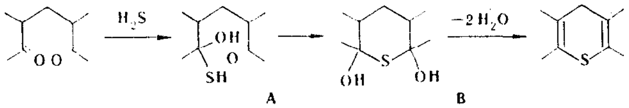
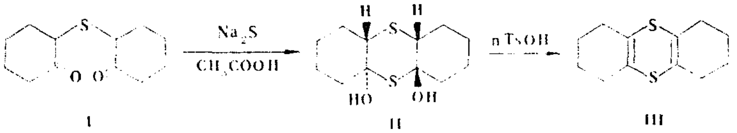
In [1] it was shown that 4H-thiapyrans, thiapyrylium salts, or thiacyclohexanes are formed in the reaction of 1,5-diketones with hydrogen sulfide, depending on the reaction conditions. A reaction mechanism that includes the intermediate formation of geminal hydroxy thiol A and glycol B was proposed. However, compounds of the A or B type could not be isolated in individual form.



We carried out the reaction between 2,2'-dicyclohexanonyl sulfide (I) and hydrogen sulfide by adding, at 0°C, an aqueous solution of sodium sulfide to an acetic acid solution of the 1,5-diketone and obtained a glycol, viz., 4a,6a-dihydroxyperhydrothianthrene (II), in almost quantitative yield in the form of colorless crystals with mp 141-144°C.



The results of elementary analysis and the IR and PMR spectroscopic data confirmed the formula presented above. Analysis of the PMR spectrum of 4a,6a-dihydroxyperhydrothianthrene made it possible to assign a trans,syn,cis configuration to it. PMR spectrum (in $CDCl_3$): 4.35 (s, 2OH), 3.36 (m, broad, 20 Hz, S—CH), 2.54 (m, broad, 8 Hz, S—CH), and 1.3-2.2 ppm (m, 16H).

When glycol II is refluxed in benzene in the presence of p-toluenesulfonic acid, it undergoes smooth conversion to the known sym-octahydrothianthrene (III) [2], whereas when it is treated with concentrated H_2SO_4 it forms the bright-red sym-octahydrothianthrene cation radical, the EPR spectrum of which is a septet with an intensity ratio of 1:2:3:4:3:2:1; this indicates interaction of the free electron with both sulfur atoms.

LITERATURE CITED

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2. J. D. London, L. B. Joung, and A. A. Robertson, J. Chem. Soc., No. 3, 591 (1964).

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