

Chemistry Laboratories, Indiana University

Synthesis of an Unsymmetrically Substituted 1,3,5-Trithiane (1)

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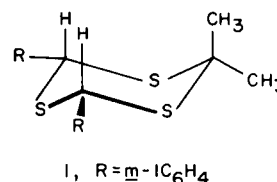
Sir:

Although 2,4,6-symmetrically substituted 1,3,5-trithianes are readily available by trimerization of thioaldehydes and thioketones (2) only one 1,3,5-trithiane, unsymmetrically substituted on carbon, had been previously reported (3). In this example, 1,3-diphenylpropane-2,2-dithiol was condensed with benzaldehyde to produce a mixture *cis* and *trans* isomers of 2,2-dibenzyl-4,6-diphenyl-1,3,5-trithiane, which could be separated chromatographically and identified by the characteristic n.m.r. peaks for axial and equatorial oriented trithiane ring protons. The mechanism of formation of this material is not clear, but must involve partial decomposition of the *gem*-dithiol, to account for the source of the extra sulfur atom in the product.

A mechanism for 1,3,5-trithiane formation has been proposed (4) which involves a *gem*-dithiol, or incipient *gem*-dithiol, as an active monomeric intermediate. This species, on further reaction with carbonyl groups could form an open-chain trimer which could either cyclize or polymerize. It is therefore reasonable to expect that if a mixture of two different carbonyl compounds is treated under conditions of trithiane preparation, the monomeric precursors which are formed may yield a mixture of symmetrically and unsymmetrically substituted 1,3,5-trithianes. The composition of the mixture of trithianes formed will depend on statistical, thermodynamic, and steric factors.

When a mixture of two equivalents of *m*-iodobenzaldehyde and one equivalent of acetone was dissolved in ethanol and saturated with hydrogen sulfide and dry hydrogen chloride, the crude precipitate which formed showed three spots when developed on thin layer chromatography plates, using a 250 μ layer of silica gel G. Merck, and a 9:1 cyclohexane-ether solvent system. Separation of the components chromatographically yielded α - and β -2,4,6-tris(*m*-iodophenyl)-1,3,5-trithianes identified by analysis, molecular weight and characteristic n.m.r. (5). The third component, R_f 0.31, was a white crystalline solid, $C_{16}H_{16}I_2S_3$, m.p. 212-212.5°, with n.m.r. peaks (acetone- d_6) at $\tau = 4.72, 8.13$ and 8.32 in a ratio of 2:3:3. The peak at 4.72 τ is characteristic of axial trithiane ring protons, and those at 8.13 and 8.32 τ are characteristic of

axial and equatorial methyl groups (6), confirming the structure of the product as 2,2-dimethyl-4,6-bis(*m*-iodophenyl)-1,3,5-trithiane, I. Several repetitions of the above experiment always resulted in the formation of the same three products, in a ratio of about 20% α -2,4,6-tris-



(*m*-iodophenyl)-1,3,5-trithiane, 40% β -2,4,6-tris(*m*-iodophenyl)-1,3,5-trithiane and 40% of I.

Since no trithioacetone nor 2,2,4,4-tetramethyl-6-aryl-1,3,5-trithiane was observed, it is apparent that the trimerization reaction must be somewhat selective. This implies that the active monomeric species derived from either *m*-iodobenzaldehyde or acetone only reacts further with aldehyde. Experiments to determine the nature of the reactive species and reasons for this selectivity are under way.

REFERENCES

- (1) Contribution No. 1500 from the Chemistry Laboratories of Indiana University, taken in part from the Ph.D. thesis of M. G., October, 1963. We are indebted to Mead Johnson and Co., Evansville, Indiana, for partial support of this work.
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