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New Reactions with Thioketone S-Sulfides and S-Disulfides

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The long-standing interest in thiosulfines such as 1 in our laboratory and elsewhere has more recently been supplemented with an interest in thiocarbonyl S-disulfides 2 which appear to be in equilibrium with 1 and their parent compounds 3, eqn. (1).^[1]

We have found^[2] that the thiosulfines 1 which can be prepared from the corresponding acetyl α-chloroalkyl disulfide precursors by «unzipping» with a nucleophile such as morpholine are subject to the disproportionation (1) and that the corresponding *cis*- and *trans*-1,2,4-trithiolanes can be formed from 1 and 3 and *cis*- and *trans*-1,2,4,5-tetrathianes by non-concerted dimerization of 1.

Moreover, we have found^[2s] that the thioketone S-sulfides 1 apparently are able to act as 1,5-dipoles with formation of unsymmetrical dimers such as 4 in an unprecedented [3+5] cycloaddition of the Woodward-Hoffmann allowed type [x4, + x6,].

Finally, extensive sulfur scrambling involving 1, 2, and/or 3 also occurs under our remarkably mild conditions with formation of hexathiepanes such as 5.^[2b]

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