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1-Alkynyl Disulfides and their 1-Thiopropargyl-3-Thiaallenyl Rearrangements

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1-ALKYNYL DISULFIDES AND THEIR 1-THIAPROPARGYL-3-THIAALLENYL REARRANGEMENTS

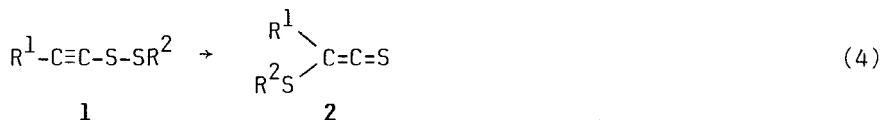
KIM NØRKJÆR and ALEXANDER SENNING

Kemisk Institut, Aarhus Universitet, DK-8000 Århus C, Denmark

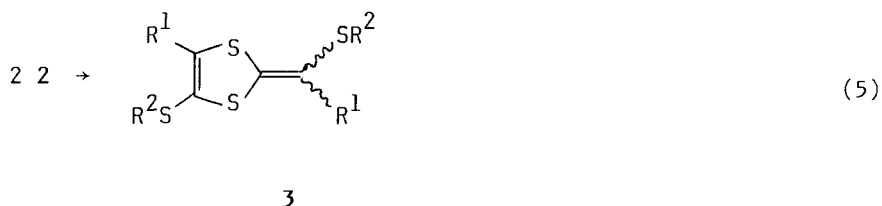
Twelve new 1-alkynyl disulfides, $R^1-C\equiv C-S-S-R^2$, **1**, for the first time including aromatic examples, have been prepared according to eqns. (1/2) and/or (3) and characterized.



It was also shown that the reported synthesis of bis(2-phenylethynyl) disulfide **1** ($R^1 = R^2 = C_6H_5$)² is in error. Of these twelve **1**, six possess unlimited shelf life while the remainder rearrange to the corresponding thio substituted thioketenes^{3,4} **2** via a [1,3]-sigmatropic shift⁵ [eqn. (4)].



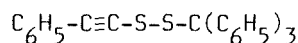
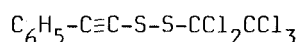
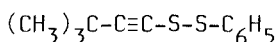
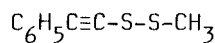
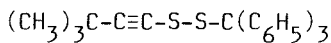
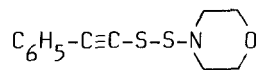
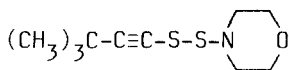
One of these thioketenes reacts further to form an unsymmetric dimer **3** [eqn. (5)],



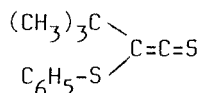
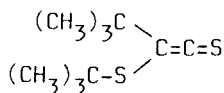
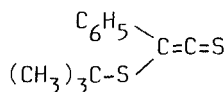
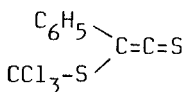
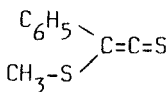
two others form α -dithiones **4** via a second [1,3]-sigmatropic shift [eqn. (6)].



We have characterized the following 1-alkynyl disulfides **1**:



and the following thio substituted thioketenes **2**:



A full account of our work has been submitted to Chem. Ber.

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