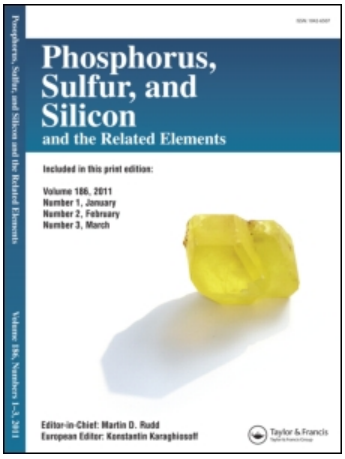

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1-Alkynyl Disulfides and their 1-Thiapropargyl-3-Thiaallenyl Rearrangements

Kim Nørkjær[a]; Alexander Senning[a]
[a] Kemisk Institut, Aarhus Universitet, Arhus C, Denmark

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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,[1] R^1-C≡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.

$$R^1C{\equiv}CLi + 1/8\ S_8 \rightarrow R^1C{\equiv}CSLi \qquad (1)$$

$$R^1C{\equiv}CSLi + R^2SCl \rightarrow \mathbf{1} \qquad (2)$$

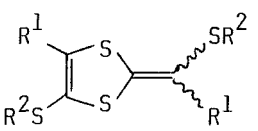
$$R^1C{\equiv}CLi + R^2SSCl \rightarrow \mathbf{1} \qquad (3)$$

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 shift[5] [eqn. (4)].

$$\underset{\mathbf{1}}{R^1\text{-}C{\equiv}C\text{-}S\text{-}SR^2} \rightarrow \underset{\mathbf{2}}{\begin{matrix} R^1 \\ \diagdown \\ R^2S \end{matrix}\!\!>C{=}C{=}S} \qquad (4)$$

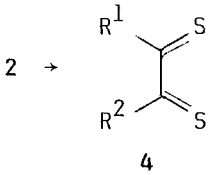
One of these thioketenes reacts further to form an unsymmetric dimer **3** [eqn. (5)],

$$2\ \mathbf{2} \rightarrow \underset{\mathbf{3}}{\text{1,3-dithiole-2-ylidene derivative}} \qquad (5)$$



3

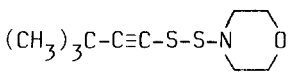
two others form α-dithiones **4** via a second [1,3]-sigmatropic shift [eqn. (6)].

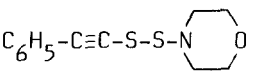


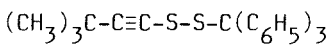
(6)

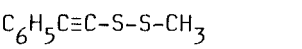
4

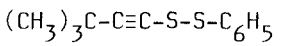
We have characterized the following 1-alkynyl disulfides **1**:

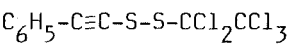


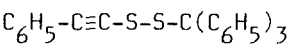




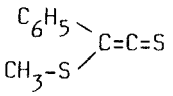


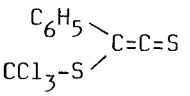


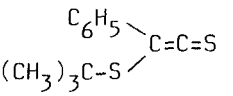


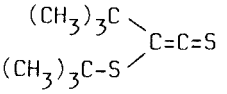


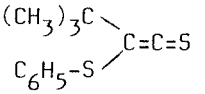
and the following thio substituted thioketenes **2**:











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

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