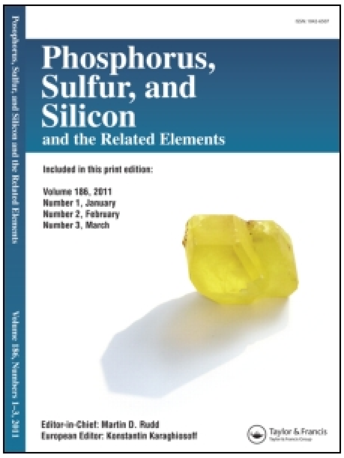

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Approaches to the Liberation of Thiosulfines

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APPROACHES TO THE LIBERATION OF THIOSULFINES

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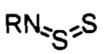
Abstract In 1979 A. Senning found a series of reactions that involve probably thiosulfines or thiocarbonyl *S*-sulfides. Now, disulfide **5a** was chosen for a re-examination, as no rearrangements seem to be involved. F, Cl, Br, CH_3, and CH_3O are used to change the electronic influence of its rings. It turns out that under the given conditions the reaction path remains unchanged. If the reaction is quenched within 5 min, high yields of the interception products are obtained. Without quenching it starts to decompose into three main products within the next hours. Piperidine is tested, too.

INTRODUCTION

Starting from SO_2, there are seven possible classes of reactive organic heterocumulenes, if we replace one or both of its oxygen atoms by groups like CR_2, NR or S. For all but one of them, isolated representatives are known, remarkably even N-thiosulfinyl amines **1**.[1,2] On the other hand, the exploration of thiosulfines **2a** or thiocarbonyl *S*-sulfides **2b** is still confined to prove their existence as reactive intermediates,[3,4] in particular by rearrangements,[5,6] additions,[5,6] elegant inter- and intramolecular 1,3-dipolar cycloadditions,[7,8,9] and intramolecular [5 + 2] cycloadditions.[10] Tranformations between them and dithiiranes **3** have been discussed, too. Recently, the isolation of compounds with a dithiirane skeleton has been reported.[11] Several times thiosulfines and dithiiranes have been postulated to form 1,2,4,5-tetrathianes **4** by dimerization.[12]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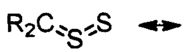
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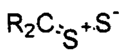
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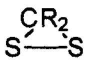
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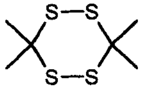
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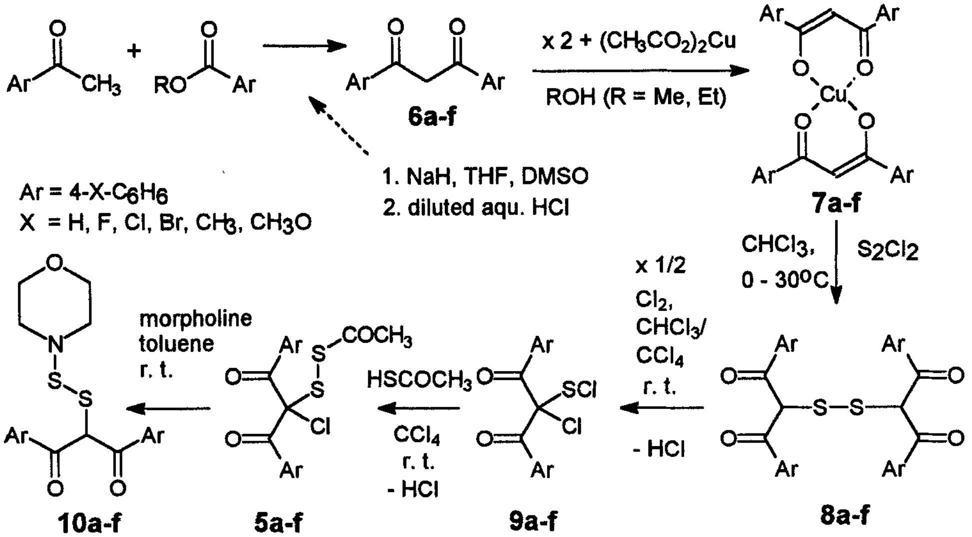
RESULTS

The present study begins with the synthesis of compounds similar to the interesting acetyldibenzoylchlormethyl-disulfide[5,6,13] **5a** (X = H) in order to see the influence on the reaction-path. For this reason the 4-aryl substituted diketones **6b-f** have been prepared by modifying a very efficient procedure.[14] They are transformed into greenish complexes **7a-f**. This serves as a cleaning and activating step for the following nucleophilic substitution by S_2Cl_2. The disulfides **8a-f** are obtained in fair yields using fractional crystallizations for their purification. In the reaction mixture always the ketone form dominates, in the course of time also the enol form arrives. In some cases by fractional crystallization the enol form could be isolated. This was the case for **8c** und **8d**. The possibility of tautomeric transformations leads generally to higher melting point intervals - with the exception of **8f**. After a short time chlorination (5 - 10 min), careful removal of chlorine traces by a strong stream of argon and partial removal of the solvent, sulfenyl chlorides **9a-f** are obtained and immediately transformed into disulfides **5a-f**, by the action of thioacetic acid. Contrary to the known procedure no heating at all was necessary and the reaction was finished already within 5 minutes. The disulfides can be crystallized by concentrating solvent-mixtures from ether and toluene. As the final step, the reaction with morpholine leads to the corresponding sulfenamides **10a-f**, probably via thiosulfines. The reaction mixtures should be quenched within 5 minutes as the products are formed probably within the first seconds and start to decompose later on. In the course of the next hours 3 dominating decomposition products could be detected by TLC. The spectroscopic properties - ^{1}H-nmr and ^{13}C-nmr - are in line with **10a**. One attempt was made to react **5a** with piperidine. From its nmr signals (6.10 ppm and 69.6 ppm, ^{13}C) a similar reaction product is probable. With the experiences gained in these experiments, it will be interesting to try 1,3-dipolar cyclo-additions with thiofluorenone to decide on the way of the reaction-path.



^{1}H-nmr for: C<u>H</u> of **8a-f**: 6.51, 6.46, 6.42, 6.34, 6.31, 6.18, and of **10a-f**: 5.98, 5.93, 5.83, 5.99, 5.99, 5.91. ^{13}C-nmr for: <u>C</u>S of **8a-f**: 65.3, 65.2, --, 65.0, 65.8, 65.8, and of **5a-f**: 86.6, 86.2, 85.8, --, 87.1, 87.7, and of **10a-f**: 68.7, 69.6, 69.2, 69.0, 68.9, 69.9.

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W. Franek had the honour to work in the laboratory of A. Senning from 11/88 to 2/89.
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