The Fluoride Anion-Catalyzed Sulfurization of Thioketones with Elemental Sulfur Leading to Sulfur-Rich Heterocycles: First Sulfurization of Thiochalcones †

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† Dedicated to Professor Janusz Jurczak (Warsaw) on the occasion of his 80th birthday.

Abstract: Fluoride anion was demonstrated as a superior activator of elemental sulfur (S8) to perform sulfurization of thioketones leading to diverse sulfur-rich heterocycles. Due to solubility problems, reactions must be carried out either in THF using tetrabutylammonium fluoride (TBAF) or in DMF using cesium fluoride (CsF), respectively. The reactive sulfurizing reagents are in situ generated, nucleophilic fluoropoly sulfide anions FS8−x− , which react with the C=S bond according to the car-bophilic addition mode. Dithiiranes formed thereby, existing in an equilibrium with the ring-opened form (diradicals/zwitterions) are key-intermediates, which undergo either a step-wise dimerization to afford 1,2,4,5-tetrahianes or an intramolecular insertion, leading in the case of thio derivatives of 2,2,4,4-tetramethylcyclobutan-1,3-dione to ring enlarged products. In reactions catalyzed by TBAF, water bounded to fluoride anion via H-bridges and forming thereby its stable hydrates is involved in secondary reactions leading, e.g., in the case of 2,2,4,4-tetramethylthiothiacyclobutane-1,3-dione to ring enlarged products. All reactions occur under mild conditions and can be considered as attractive methods for the preparation of sulfur rich heterocycles with diverse ring-size.

Keywords: thioketones; thiochalcones; fluoride anion; elemental sulfur; sulfur heterocycles

1. Introduction

It is a well-known fact that large amounts of elemental sulfur (S8) are available as a side product of diverse technological processes, and its further usage in a sustainable cycle of conversions leading to useful, organic compounds represents an important and challenging problem for chemical industry and related branches [1]. Sulfurization reactions performed with elemental sulfur and leading to cyclic or acyclic organic compounds constitute an interesting and practically relevant topic in the current organic chemistry of sulfur. Results, which were mainly published in the recent two decades, are summarized and compared in an excellent, comprehensive review [2].

Reactions of thiocarbonyl compounds with elemental sulfur and their conversion into sulfur-rich heterocycles attract attention since many decades. Aromatic, aliphatic/ aromatic...
or cycloaliphatic thioketones 1, and 2, e.g., thiobenzophenone (1a) and (tert-butyl) phenyl thioketone (1b), as well as cycloaliphatic analogues such as 2,2,4,4-tetramethylcyclobutane-1,3-dithione (2a), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (2b) or adamantanethione (2c) are known to undergo sulfurization in the presence of a nucleophilic catalyst or upon heating without a catalyst in an appropriate organic solvent [3–8] (Figure 1). On the other hand, sulfurization of thioaldehydes 3 (α,β-unsaturated thioketones) as substrates for the preparation of sulfur-rich heterocycles has not yet been reported.

![Figure 1. Aromatic and cycloaliphatic thioketones 1 and 2, and thioaldehydes 3 applied in the study.](image)

In many cases, the mechanistic interpretation of the observed reactions course was based on the assumption that the transient thiocarbonyl S-sulfides (thiosulfines) 4 [9], generated via the transfer of a sulfur atom to the C=S bond, and considered as ‘sulfur-rich’ representatives of so called ‘sulfur-centered 1,3-dipoles’, play the crucial role in the formation of sulfur heterocycles, such as the corresponding 1,2,4-trithiolanes 5 [10] (Figure 2). On the other hand, the larger rings, e.g., 1,2,4,5-tetrathianes 6 or 1,2,3,5,6-pentathiepanes 7, are formed via more complex processes, but the reaction mechanisms are not fully rationalized to date and require further studies [3,4,11].

![Figure 2. Thiocarbonyl S-sulfides 4, the sulfur-rich heterocycles 1,2,4-trithiolanes 5, 1,2,4,5-tetrathianes 6, and 1,2,3,5,6-pentathiepanes 7, as well as phenylpolysulfide anions 8A.](image)

For example, in some instances, sulfurization of thietoketones performed in the presence of a nucleophilic catalyst, e.g., sodium or potassium thiophenolate, were explained via involvement of in situ-generated, reactive polysulfide anions of type 8A [3,4]. Thus, Huisgen and Rapp reported that elemental sulfur reacts with thiobenzophenone (1a) in boiling acetone, in the presence of catalytic amounts of sodium thiophenolate, yielding 3,5,6,6-tetraphenyl-1,2,4,5-tetrathiane (6a) (R = Ph) as the exclusive product [3]. The same authors demonstrated that 3-thioxo-2,2,4,4-tetramethyl-cyclobutanone (2b) [4] and adamantanethione (2c) [3] also undergo sulfurization under the same conditions. However, the isolated products are either the bis-spiro cyclic 1,2,4,5-tetrathianes 6b/6c (R,R = 6b: spiro-2,2,4,4-tetramethyl-3-oxocyclobutyl; 6c: spiro-2-adamantyl) or 1,2,3,5,6-pentathiepanes 7a/7b (R,R = 7a: spiro-2,2,4,4-tetramethyl-3-oxocyclobutyl; 7b: spiro-2-adamantyl), respectively.

Okuma also studied reactions of 2c with elemental sulfur in the presence of catalytic amounts of triphenylphosphine sulfide (Ph3P=S) in boiling CHCl3 and isolated...
1,2,4-trithiolane 5c (R, R = spiro-2-adamantyl) in 59% yield [5]. In the same publication, sulfurization of 1a with elemental sulfur in boiling xylene, in the presence of maleic anhydride as a trapping reagent for the postulated, intermediate thiobenzophenone S-sulfide (4a) (R1 = R2 = Ph), was also described, and the expected [3+2]-cycloadduct, i.e., 5,5-diphenyl-1,2-dithiole-3,4-dicarboxylic acid anhydride, was obtained in 74% yield [5].

Nakayama et al. performed sulfurization of the cycloaliphatic thioketone 1b with elemental sulfur without a nucleophilic catalyst using DMF or toluene as a solvent. Depending on the solvent, either a mixture of the isomeric 1,2,4-trithiolanes cis- and trans-5a (boiling toluene) or cis-5a as the sole product (DMF, rt), were obtained [6, 7]. In these reactions, a plausible mechanistic explanation comprised the in situ-formation of thiocarbonyl sulfide 1b and its subsequent stereoselective [3+2]-cycloaddition onto the unconverted thioketone 1b (Scheme 1).

Scheme 1. Reaction of tert-butyl phenyl thioketone (1b) with elemental sulfur S8 in boiling toluene or in DMF at rt (ref. [6, 7]).

A similar reaction performed with tert-butyl 4-methylphenyl ketone in boiling pyridine and using tetraphosphorus decasulfide (P4S10) as a thionating and sulfurizing reagent, was described by Okuma et al. [8].

In spite of the fact that the fluoride anion is well known as a useful reagent acting not only as a unique catalyst for nucleophilic trifluoromethylation reactions [12], as a desilylating agent [13], but also as a strong base [14], its exploration as an activating reagent for elemental sulfur in the sulfur transfer reactions is limited to two reports only, which are known to date [15, 16]. In one of them, Petrov and Marshall demonstrated the utility of the fluoride anion as a potent activator of elemental sulfur used for in situ-generation of reactive hexafluorothioacetone S-sulfide, which subsequently was trapped by ethylenic dipolarophiles yielding corresponding bis-trifluoromethylated 1,2-dithioles in high yields [15]. In the second publication, sulfurization of cyclopropenethione 2d and its oxo-analogues with elemental sulfur in DMF solution at room temperature was described [16] (Scheme 2). In this study, potassium fluoride was used in two-fold excess as activator and the molar ratio of reagents 2d/[S]/KF was optimized to 1:2:2. Under these conditions, 3-thioxo-1,2-dithiole 9 was obtained as the product of a cascade reaction and isolated in good yield (84%). A series of analogous Se-heterocycles was also obtained using elemental selenium instead of sulfur [16].

Scheme 2. Fluoride anion-catalyzed sulfurization of diphenylcyclopropenethione (2d) (ref. [16]).

Unlike thioketones, similar sulfurization of α,β-unsaturated thioketones 3 (thiochalcones) with S8 are almost unknown. In an earlier publication, however, sulfurization of rather complex thiochalcones 11, prepared in situ from corresponding ketones 10, was carried out in non-polar xylene by treatment with S8. These reactions led to the polycyclic products 12, which were formed as minor products, exclusively [17] (Scheme 3). The formation of the latter heterocycles was explained via a multi-step mechanism with the respective α,β-unsaturated thiocarbonyl S-sulfides 4c as the reactive intermediates in the postulated intramolecular [5+2]-cycloaddition reactions.
The main goal of the present study was examination of the utility of the fluoride anion as a new type of a catalyst for sulfurization of thiobenzophenone (1a) and cycloaliphatic thioketones 2a–2c. In extension of the study with thioketones, first sulfurization reactions of selected thiochalones 3a–3d were carried out by using elemental sulfur (S₈) in the presence of a nucleophilic catalyst. Elucidation of the mechanisms of the studied reactions, leading to the formation of sulfur-rich heterocycles with diverse ring size, was of primary interest.

2. Results and Discussion

2.1. Conversions of Thioketones 2a and 2b upon Treatment with Catalytic Amounts of TBAF in the Absence of Elemental Sulfur

In an earlier publication, unexpected conversions of thiobenzophenone (1a) and cycloaliphatic thioketones 2a–2c upon treatment with catalytic amounts of TBAF in THF solution were reported [18]. The obtained results demonstrated that the type of products formed in each reaction strongly depended on the type of thioketone used in the studied experiment. Interestingly enough, two structurally similar cycloaliphatic thioketones 2a and 2b—derived from 2,2,4,4-tetramethylcyclobutane-1,3-dione (13)—gave completely different sets of products. Whereas in the case of dithione 2a the only product was the isomeric thiolactone 14, the monothione 2b afforded a mixture of the unusual dithiocarboxylate 15 and the parent dione 13 (Scheme 4).

Due to the importance of this observation, both experiments were repeated in the initial stages of the present study. The already described isomerization of 2a leading to 14 as the sole product was fully confirmed. However, in the experiment with 2b we found that along with 13 and 15 also the ring-enlarged five-membered dithiolactone 16b was present in the crude mixture. Moreover, the molar ratio of dione 13 and dithiolactone 16b...
was ca. 1:1 and this finding suggests that the monothione \(2b\) can be an actual source of sulfur incorporated into the four-membered ring of another molecule of the same substrate.

The mechanism of the isomerization of \(2a\) induced by fluoride anion presented in [18] is a plausible explanation of this conversion. On the other side, the formation of dithioester \(15\), which requires reduction of the \(\text{C}=\text{S} \) bond of \(2b\), as well as the intermolecular transfer of the sulfur atom from one molecule of \(2b\) to another one in the formation of \(16b\), has not convincingly been rationalized yet. Searching for a correct explanation, an additional experiment with attempted conversion of \(2b\) using catalytic amounts of flame-dried CsF in dry DMF has also been performed. To our surprise, no effect was observed even after ca. 2 h at rt. This situation changed immediately after addition of a drop of water to the solution, which rapidly changed the color to orange indicating thereby conversion of \(2b\). Subsequent control of the composition of products by means of \(^1\text{H}-\text{NMR}\) spectroscopy confirmed the formation of the mixture of three known products, namely \(13, 15,\) and \(16b\). This result clearly demonstrated that the unexpected conversion of \(2b\) can be performed only in the presence of water and the involvement of the hydrated fluoride anion in the reaction solution plays a crucial role in the formation of \(15\) and \(16b\). Notably, TBAF is known to exist as a hydrated complex and the complete removal of water requires a special procedure [19].

2.2. Activation of Elemental Sulfur with Fluoride Anion

It is very likely that the activation of elemental sulfur with fluoride anion comprises cleavage of the \(S_8\)-ring leading to a mixture of red-colored, highly nucleophilic fluoropoly sulfide anions \(8B\) with variable length of the sulfur chain \(S_x\) (Scheme 5).

![Scheme 5](attachment://Scheme_5.png)

**Scheme 5.** Ring cleavage of the \(S_8\) crown and formation of a mixture of fluoropoly sulfide anions \(8B\).

It is worth of mentioning that in the case of TBAF complete removal of water forming ‘fluoride anion hydrates’ is a difficult problem and some amounts of water are still present in the solution [20]. In contrast, cesium fluoride, which can be used alternatively as a source of the fluoride anion, can be prepared as a water-free salt. However, due to solubility problems reactions with CsF have to be performed in dry DMF solution. In the sulfurization reaction of a thio ketone, the \(\text{C}=\text{S} \) bond is believed to react with anions \(8B\) according to the ‘carbophilic’ mode of the initial nucleophilic attack.

2.3. Sulfurization of Thio ketones with Elemental Sulfur

All experiments were carried out using optimized protocols elaborated in a series of preliminary test reactions. Magnetically stirred suspension of elemental sulfur in THF at rt dissolved immediately after addition of catalytic amounts of TBAF, and the obtained solution was colored red or olive-green, thereby indicating formation of fluoropoly sulfide anions \(8B\) with variable length of the \(S_x\) chain. Addition of a thio ketone led to the change of the color within a few minutes, and the completion of the reaction was established by TL C (see Tables 1 and 2). After pre-purification by column chromatography aimed at separation of the catalyst, the crude mixtures were analyzed in the \(^1\text{H}-\text{NMR}\) spectra with weighted standard (1,2-dichloroethane; Method A), and pure products were isolated on preparative plates (Method B). Alternatively, selected reactions were performed in DMF solution using pre-dried CsF as a catalyst.
Table 1. Sulfurization conditions of thioketones 2a and 2b and yields of the products.

<table>
<thead>
<tr>
<th>Thioketone</th>
<th>Entry</th>
<th>RT [h], rt</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>A</td>
<td>1</td>
<td>14</td>
<td>63 (^a)</td>
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<td></td>
<td>16a</td>
<td>11 (^a)</td>
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<td>16a</td>
<td>8 (^b)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>6e</td>
<td>15 (^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>meso-17,D,L-17</td>
<td>43 (^b)</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>2</td>
<td>14</td>
<td>9 (^a)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>18</td>
<td>5 (^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7c</td>
<td>23 (^b)</td>
</tr>
<tr>
<td></td>
<td>C'</td>
<td>24</td>
<td>7c</td>
<td>54 (^b)</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>2</td>
<td>14</td>
<td>3 (^a)</td>
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<td>16a</td>
<td>5 (^a)</td>
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<td></td>
<td>7c</td>
<td>46 (^b)</td>
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<td></td>
<td>19</td>
<td>4 (^b)</td>
</tr>
<tr>
<td>2b</td>
<td>A</td>
<td>1.5</td>
<td>15</td>
<td>30 (^a)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>16b</td>
<td>10 (^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6b</td>
<td>12 (^a)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3</td>
<td>15</td>
<td>20 (^a)</td>
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<td></td>
<td>16b</td>
<td>23 (^a)</td>
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<td></td>
<td></td>
<td>6b</td>
<td>40 (^a)</td>
</tr>
<tr>
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<td>C</td>
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<td>7a</td>
<td>34 (^b)</td>
</tr>
<tr>
<td></td>
<td>C'</td>
<td>24</td>
<td>7a</td>
<td>43 (^b)</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>22</td>
<td>7a</td>
<td>52 (^b)</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>6</td>
<td>7a</td>
<td>60 (^b)</td>
</tr>
</tbody>
</table>

\(^a\) Method A (\(^1\)H-NMR); \(^b\) Method B (isolated products).

Table 2. Sulfurization conditions of thioketones 2c and 1b and yields of the products (isolated amounts).

<table>
<thead>
<tr>
<th>Thioketone</th>
<th>Entry</th>
<th>RT (h)</th>
<th>Product</th>
<th>Yield (%)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2c</td>
<td>A</td>
<td>72</td>
<td>5c</td>
<td>59</td>
<td>7b</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>46</td>
<td>-</td>
<td>-</td>
<td>7b</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>24</td>
<td>-</td>
<td>-</td>
<td>7b</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>C'</td>
<td>24</td>
<td>5c</td>
<td>59</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1b</td>
<td>B</td>
<td>72</td>
<td>6a</td>
<td>28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>72</td>
<td>6a</td>
<td>52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C'</td>
<td>48</td>
<td>6a</td>
<td>56</td>
<td>-</td>
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</tr>
</tbody>
</table>

2.3.1. Sulfurization of ‘Dithione’ 2a and ‘Monothione’ 2b

A series of experiments aimed at determination of the impact of the molar ratio of 2a to sulfur on the structure of the formed products, was performed starting with 1:0.5, 1:1, 1:2, 1:4 or 1:8 (Entries A–E) mixtures of the two reagents. In the obtained crude mixtures both, known and hitherto unknown sulfur-rich heterocycles were initially identified by \(^1\)H-NMR spectroscopy (see Supplementary Materials part) and subsequently isolated as pure compounds (Figure 3).

In the first experiment, the reaction with a 1:0.5 molar ratio of 2a and atomic [S] (Entry A) led to a mixture of the isomeric thiolactone 14 (63% yield) and the ring enlarged five-membered thiolactone 16a (11%) (Figure 3, Table 1).
More important information was found in the 13C-NMR spectrum, which revealed approximately the same intensities located at 1.32, 1.35, 1.51, 1.51, 1.69, 1.71, 1.74, and 1.75 ppm. More important information was found in the 13C-NMR spectrum, which revealed the presence of two isomeric compounds with very similar patterns of absorptions. The most characteristic ones were those found at 248.18 and 248.39 ppm, which were attributed to two C=S groups of the dithiocarboxylate type. In addition, two signals at 78.54 and 78.71 ppm corresponded to non-equivalent C\(_{sp3}\) atoms connected with two sulfur atoms. In analogy to the \(^1\)H-NMR, eight signals between 26.32 and 30.66 ppm suggested the presence of structurally similar 16 Me groups. The elemental analysis confirmed the molecular formula C\(_{16}\)H\(_{24}\)S\(_6\), which can be attributed to a 1:1-mixture of the isomeric bis-spiro-1,3-dithietane derivatives meso- and d,l-17. All attempts to separate this mixture to obtain pure diastereoisomers, either by chromatography or fractional crystallization, were unsuccessful.

The less polar fraction formed a yellowish oil, which in the \(^1\)H-NMR spectrum showed the presence of only two broadened singlets located at 1.42 and 1.69 ppm. More information delivered the \(^13\)C-NMR spectrum with two low field absorptions at 243.0 and 216.6 ppm. Whereas the first signal could be attributed to the C=S group incorporated in the four-membered ring of cyclobutane, the second one was identified as the C=O unit of a cyclobutane moiety. In addition, two closely located signals with low intensity, found at 79.86 and 79.91 ppm, respectively, revealed the presence of two C\(_{sp3}\)-atoms attached to two S-atoms like in the molecule of a 1,2,4,5-tetrathiane. As a matter of fact, elemental analysis confirmed the molecular formula C\(_{16}\)H\(_{24}\)O\(_5\)S\(_5\), which corresponds to the structure of the ‘non-symmetric’ dispiro-1,2,4,5-tetrathiane 6e (Figure 3, Table 1). Apparently, the initially formed ‘symmetric’ analogue 6d (not isolated) underwent hydrolysis in the reaction solution and one C=S group was converted into the C=O moiety.

Finally, the smallest and least polar fraction isolated after chromatography was identified as the known [4], five-membered dithiolactone 16a (8%) (Table 1).

Increase of the molar excess of sulfur to 4 mol-equiv. (Entry D) changed dramatically the composition of the product mixture, and in this case the major fraction consisted of an orange oil, which in the \(^1\)H-NMR spectrum showed a complicated pattern of signals

Figure 3. Products of sulfurization of thioketones 2a and 2b with elemental sulfur in the presence of TBAF in THF solution.
was identified as the known five-membered dithiolactone 18 (thiosulfines) for the oxo analogue ppm, respectively. In another experiment carried out with 2a and [S] in a ratio 1:2 (Entry C), pentathiepane 7c was isolated in a lower yield (23%) and the already described sulfur heterocycles 14 (9%), 16a (8%), and 18 (5%) were formed as side products.

Two more sulfur-rich heterocycles were separated as minor products. One of them was identified as the known five-membered dithiolactone 18 [21], and the structure of the second one was elucidated based on spectroscopic data and elemental analysis as hitherto unknown spirocyclic 1,2,3,4,5,6-hexathiepane 19 being a thioxo analogue of the corresponding oxo derivative, which was described in our earlier work [22]. Both compounds revealed very similar chemical shifts for the spiro-C-atoms: 95.6 (for 19) and 92.2 (for the oxo analogue [22]) ppm, respectively.

Notably, the same pentathiepane 7c was isolated chromatographically in 54% yield as the sole product when the sulfurization of 2a was carried out in DMF solution using dried CsF as a catalyst (Entry C′). In that experiment the molar ratio of 2a and [S] was calculated to 1:2.

In contrast to the hitherto unexplored dithione 2a, its monothione analogue 2b was studied extensively by Huisgen and Rapp in sulfurization reactions with elemental sulfur using potassium thiophenate as a catalyst [4]. The main goal of that study was the elucidation of the mechanism of the dimerization of in situ-generated intermediates leading to 1,2,4,5-tetrathiane 6b. In our hands, reactions of 2b with variable amounts of sulfur and performed with TBAF as a catalyst led virtually to similar products. Thus, in experiments starting with 2b and [S] in a molar ratio 1:0.5 (Entry A) or 1:1 (Entry B), the only sulfur-rich compound identified in the crude mixture of products was 6b accompanied by the above reported 3-oxopentanedithioate 15 and dithiolactone 16b. In the 1:1 experiment, the yield of tetrathiane 6b was higher (40%) (Table 1). Further enhancement of the amounts of sulfur to 1:2 (Entry C), 1:4 (Entry D), and finally 1:8 (Entry E) molar ratio suppressed completely the formation of other products and nothing but 1,2,3,5,6-pentathiepane 7a was isolated in acceptable yields of 34%, 52%, and 60%, respectively. In a test experiment using pre-dried CsF (instead of TBAF) in DMF solution and starting with a 1:2 ratio of 2b and atomic [S], the latter heterocycle was isolated in 43% yield (Entry C′). Spectroscopic and physicochemical data of 7a fitted well with those reported earlier [4]. In addition, the crystal structure of this compound showing a complex conformation of this seven-membered, sulfur-rich heterocycle has also been reported in another publication [22]. In the present study, the structure of 7a was redetermined by X-ray analysis and the crystallographic characterization of this sulfur-rich heterocycle could be refined thereby.

2.3.2. Formation of Sulfur-Rich Heterocycles from Thioketones 2a and 2b; Mechanistic Interpretations

It has to be underlined that in both series of experiments performed either with 2a or 2b and starting with a 1:0.5 molar ratio of a thioketone 2 and elemental sulfur [S], no traces at all of the corresponding 1,2,4-trithiolane of type 5 could be detected in the mixtures of products. These findings allow to exclude participation of thio carbonyl S-sulfides (thiosulfines) 4A–C derived from the studied thioketones 2 as reactive intermediates in the herein presented sulfurizations. Instead, these observations suggest to consider dithiiranes 21 and their ring opened forms, i.e., diradicals 22 (or zwitterions 23), as elusive species involved in the formation of the isolated sulfur-rich heterocycles (Scheme 6). The parent dithiirane and its isomerization to dithioformic acid can serve as a model system helpful in the formulation of experimentally well founded rational description of the complex conversions observed in the present study [23].

It seems a plausible explanation that in situ-generated fluoropolysulfide anions 8B undergo the carbophilic addition to the C=S bond forming the intermediate anion 20. The
latter extrudes a new fluoropolysulfide anion with a shortened sulfide chain yielding the elusive dithirane 21, which may exist in an equilibrium with ring opened reactive species 22 and/or 23 (Scheme 6).

Scheme 6. Initial, nucleophilic attack of fluoropolysulfide anion 8B onto the C=S bond and subsequent ring closure leading to dithiiranes 21 as elusive intermediates.

In the reaction performed with equimolar amounts of thioketone and sulfur, step-wise dimerization of the latter species leads to the formation of the 1,2,4,5-tetrathiane 6. Alternatively, the intermediate species 22 undergo ring-expansion via intramolecular insertion of the S-atom into a C–C bond to form dithiolactones 16. However, if there is a source of sulfur and fluoropolysulfide 8B exists in the system, it can transfer one more sulfur atom to the intermediate 24 yielding finally 1,2,3,5,6-pentathiepanes 7 (Scheme 7).

Scheme 7. Step-wise formation of 1,2,4,5-tetrathianes 6 and 1,2,3,5,6-pentathiepanes 7.

This interpretation seems to be more likely than an alternative pathway via a secondary ring opening/ring closure reaction sequence of the initially formed 1,2,4,5-tetrathiane derivative, after reaction with a polysulfide anion, leading either to 1,2,4-trithiolanes or 1,2,3,5,6-pentathiepanes. This pathway has been suggested in an earlier publication, dealing with similar problems of sulfurization reactions of some aromatic aldehydes [11].

The unexpected formation of diastereoisomeric dispiro-1,3-dithietane 17 deserves also a comment. It seems likely that in analogy to the earlier observed BTAFl/TMSCF3 induced dimerization of dithione 2a [18] affording 1,3-dithietane 25, also fluoropolysulfide anions 8B can catalyze an analogous reaction. Now, each of the C=S bonds can react with 8B and via addition/ring expansion sequence is converted in mixtures of isomeric, spiroheterocycles 17 (Scheme 8). Alternatively, dimerization of the initially formed dithiolactone 16a, induced by fluoride anion can be postulated. Notably, no formation of corresponding products of type 17, starting with monothione 2b was observed and this is one more feature, which differs behavior of both cycloaliphatic thio ketones in sulfurization reactions.
the symmetric 1,2,3,5,6-pentathiepane (Entry C) was formed in DMF solution at rt exclusively, when the reaction was performed with CsF. A unique product, which was found in the mixture of products as the major component (59%). The same product was also a comment. It seems likely that in analogy to the earlier observed BTAF/TMSCF in the fluoride anion catalyzed sulfurization reactions. In both cases, the reactions were carried out with TBAF as a catalyst in THF at rt, and required remarkably longer times for completion (see Table 2, Figure 4). Analysis of the crude mixtures of products by $^1$H-NMR spectroscopy and separation by preparative thin-layer chromatography led to the identification and isolation of three types of sulfur-rich heterocycles. Thus, in the case of 2c, irrespective of the molar ratio of thioketone and sulfur, 1:1 (Entry B) or 1:2 (Entry C), only the symmetric 1,2,3,5,6-pentathiepane 7b was obtained in moderate yields (37–51%). However, in the experiment with a 1:0.5 molar ratio (2c: [S], Entry A), 1,2,4-trithiolane 5c was found in the mixture of products as the major component (59%). The same product was formed in DMF solution at rt exclusively, when the reaction was performed with CsF (Entry C'). Its presence suggests the appearance of adamantane-2-thione S-sulfide and subsequent trapping by another molecule of 2c according to the [3+2]-cycloaddition mode as suggested in our earlier study [24]. Limited amounts of elemental sulfur available in the first experiment (Entry A) can suggest that the reaction leading to 5c follows a hitherto unknown mechanism of the reaction of fluoride anion with 2c mentioned in our earlier publication [18]. Nevertheless, formation of 7b can result from the mechanism initiated by the attack of fluoropolysulfide anion onto the C=S bond according to the pathways presented in Scheme 7. Notably, no symmetric 1,2,4,5-tetrathiane derived from 2c and obtained by Huisgen and Rapp [3] via sulfurization of the latter in reactions catalyzed with potassium thiophenolate, was observed in our experiments.

Scheme 8. Postulated mechanism of the formation of diastereoisomeric bis-spiro-1,3-dithianes 17 via initial dimerization of the starting thioketone 2a.

An alternative cyclization pathway of the initial anionic adduct 20, formed via attack of anions 8B onto the C=S group, leading to the hexathiepane 19, is presented in Scheme 9. It demonstrates the known tendency for the formation of seven-membered rings consisting of sulfur and carbon atoms [22].

Scheme 9. Mechanistic explanation of the formation of 1,2,3,4,5,6-hexathiepane 19.

2.3.3. Sulfurization of ‘Adamantanethione (2c) and Thiobenzophenone (1a)

In extension of the study performed with cycloaliphatic thioketones 2a and 2b, derived from the sterically crowded and ring congested 2,2,4,4-tetramethylcyclobutane-1,3-dione (13), sulfurization reactions of easily available thioketones, such as the cycloaliphatic adamantane-thione (2c) and the aromatic thiobenzophenone (1a), were also tested in the fluoride anion catalyzed sulfurization reactions. In both cases, the reactions were carried out with TBAF as a catalyst in THF at rt, and required remarkably longer times for completion (see Table 2, Figure 4). Analysis of the crude mixtures of products by $^1$H-NMR spectroscopy and separation by preparative thin-layer chromatography led to the identification and isolation of three types of sulfur-rich heterocycles. Thus, in the case of 2c, irrespective of the molar ratio of thioketone and sulfur, 1:1 (Entry B) or 1:2 (Entry C), only the symmetric 1,2,3,5,6-pentathiepane 7b was obtained in moderate yields (37–51%). However, in the experiment with a 1:0.5 molar ratio (2c: [S], Entry A), 1,2,4-trithiolane 5c was found in the mixture of products as the major component (59%). The same product was formed in DMF solution at rt exclusively, when the reaction was performed with CsF (Entry C'). Its presence suggests the appearance of adamantane-2-thione S-sulfide and subsequent trapping by another molecule of 2c according to the [3+2]-cycloaddition mode as suggested in our earlier study [24]. Limited amounts of elemental sulfur available in the first experiment (Entry A) can suggest that the reaction leading to 5c follows a hitherto unknown mechanism of the reaction of fluoride anion with 2c mentioned in our earlier publication [18]. Nevertheless, formation of 7b can result from the mechanism initiated by the attack of fluoropolysulfide anion onto the C=S bond according to the pathways presented in Scheme 7. Notably, no symmetric 1,2,4,5-tetrathiane derived from 2c and obtained by Huisgen and Rapp [3] via sulfurization of the latter in reactions catalyzed with potassium thiophenolate, was observed in our experiments.
The fluoride anion catalyzed sulfuration of thiobenzophenone (1a) was performed starting with 1:1 or 1:2 molar ratio of 1a to [S] (Entry B or Entry C, respectively). In both cases colorless products precipitated from THF solution, and the analysis of the obtained crude mixtures demonstrated that the literature known, symmetric 3,3,6,6-tetraphenyl-1,2,4,5-tetrathiane (6a) [3] was the sole product in both reactions, isolated in 28% and 52% yield, respectively. Remarkably, no ring expansion to the corresponding 1,2,3,5,6-pentathiepane in the experiment with molar excess of sulfur (1:2; Entry C) was observed. This observation suggests that this could be the effect of the limited solubility of 6a, which precipitated from the THF solution in the course of the reaction. Notably, Huisgen and Rapp did not observe formation of this 1,2,3,5,6-pentathiepane either [3]. In the present study, along with 1a, other well-known aromatic thioketones such as xanthione, thioxanthione and dibenzosuberethione, which have been frequently applied in our studies, were tested in the fluoride anion catalyzed sulfuration, but in all cases no reaction was observed at rt, even after longer reaction time (up to one week). Particularly, thiofluorenone (9H-fluoren-9-thione) converted rapidly into the dimeric fluorenyliden-9-ene (tetrabenzo[5.5]fulvalene) in analogy to the result described in [18]. Thus, thiobenzophenone (1a) should be considered as an exceptional case showing superior tendency to undergo the reaction with fluoropolysulfide anion 8B with subsequent ‘head-to-head’ dimerization of a reactive intermediate leading to tetrasubstituted 1,2,4,5-tetrathiane 6a.

In accordance with the proposal presented in Scheme 9, a plausible mechanistic interpretation of this multi-step reaction is the initial formation of the unstable 3,3-diphenyl dithiirane (21c). The latter, after spontaneous cleavage of the S=S bond, converts into a reactive intermediate of type 24, which undergoes step-wise dimerization leading to the 1,2,4,5-tetrathiane ring (Scheme 7).

2.4. Sulfurization of Thiochalcones

In contrast to thioketones 1/2, the α,β-unsaturated analogues, i.e., diaryl thiochalcones 3, are much less investigated as potentially useful reagents in the cycloaddition chemistry. In fact, thiochalcones exhibit a far more complex nature in comparison with thioketones, which comprises their tendency to form two dimeric molecules existing in an equilibrium with the monomeric ones. The equilibrium concentration of monomeric and dimeric forms depends on the solvent polarity that makes thiochalcones difficult to be tamed in [3+2]-cycloadditions [25], Diels-Alder- [26], and hetero-Diels-Alder-reactions [27]. Correctly, the fraction containing only the monomeric form is often described as ‘thiochalcone fraction’ [25,27]. As mentioned in the ‘Introduction’, the single experiment reporting sulfuration of a rather complex, in situ-generated thiochalcone relates to harsh reaction conditions with heating of the reaction mixture in boiling xylene [17].

The goal of the present study was to verify whether sulfuration of typical thiochalcones 3 can be performed under mild conditions using elemental sulfur activated by TBAF in THF at room temperature. The test experiment performed with 3a and elemental sulfur (molar ratio of 3a to [S] was 1:2) according to the protocol described above for thioketones 2a,b (Entry C), was unsuccessful, however. In that case, no conversion of 3a occurred even after three days of stirring at rt. Instead, slow decomposition of the starting 3a was observed by TLC.
Prompted by Okuma’s report [5], we decided to use PPh₃ in boiling acetone solution as a nucleophilic activator of sulfur (Procedure I, Table 3). In the cited study, comparable results were obtained using either PPh₃ or S=PPh₃. In our hands, under these conditions a part of 3a, consisting of monomeric thiochalcone and its dimer (dithiine derivative, under-went dissociation) reacted with sulfur yielding an orange-red colored, crystalline product. In the ¹H-NMR spectrum (see Supplementary Materials part), along with absorptions of aromatic H atoms, a characteristic set of two doublets with ³J_H,H = 3.0 Hz was found at 5.87 and 6.19 ppm, respectively. In addition, ¹³C-NMR revealed a signal of a C₃ atom at 63.7 ppm and two other signals located at 120.7 and 132.9 ppm, respectively, with clearly different intensities, which could be attributed to a CH=C unit. The elemental analysis confirmed the molecular formula C₁₅H₁₂S₂ expected for a product of monosulfurization of 3a. Based on the collected spectroscopic data, the structure of the obtained product was established as 3,5-diphenyl-3H-1,2-dithiole (26a, Scheme 10).

An analogous procedure has been applied to perform sulfurization of three other thiochalcones 3b–3d, which have also been converted into the desired 3H-1,2-dithioles 26b–d, albeit in all cases the yields of the isolated products were rather low. The results of all experiments aimed at the synthesis of heterocycles 26 are summarized in Table 3.

<table>
<thead>
<tr>
<th>Thiochalcone</th>
<th>Procedure</th>
<th>RT [h]</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>I</td>
<td>3.5</td>
<td>26a</td>
<td>40 a (63 b)</td>
</tr>
<tr>
<td>3a</td>
<td>II</td>
<td>4.0</td>
<td>26a</td>
<td>15 a</td>
</tr>
<tr>
<td>3a</td>
<td>III</td>
<td>0.5</td>
<td>26a</td>
<td>41 a</td>
</tr>
<tr>
<td>3a</td>
<td>IV</td>
<td>72</td>
<td>26a</td>
<td>15 a</td>
</tr>
<tr>
<td>3b</td>
<td>I</td>
<td>4.0</td>
<td>26b</td>
<td>15 a</td>
</tr>
<tr>
<td>3c</td>
<td>I</td>
<td>3.5</td>
<td>26c</td>
<td>20 a</td>
</tr>
<tr>
<td>3c</td>
<td>IV</td>
<td>72</td>
<td>26c</td>
<td>17 a</td>
</tr>
<tr>
<td>3d</td>
<td>I</td>
<td>3.0</td>
<td>26d</td>
<td>12 a</td>
</tr>
</tbody>
</table>

a Method A (isolated product); b Method B (¹H-NMR).

It has to be underlined that the ¹H-NMR analysis of the crude mixture revealed the presence of the non-reacted thiopyran as one of the dimers of the starting thiochalcone [25–27]. Apparently, this dimer is stable under the reaction conditions and does not undergo dissociation leading to new portions of the monomeric form. This fact must be taken into account while calculating the yield of the obtained sulfurization product.

An analogous procedure has been applied to perform sulfurization of three other thiochalcones 3b–d, which have also been converted into the desired 3H-1,2-dithioles 26b–d, albeit in all cases the yields of the isolated products were rather low. The results of all experiments aimed at the synthesis of heterocycles 26 are summarized in Table 3.

For comparison reasons, two modifications of the applied procedure were tested in reactions with 3a. In the first case, potassium thiophenolate was used as a catalyst, but after 4 h reaction time the product 26a was isolated in lower yield (15%) (Procedure II). The second modification comprised replacement of acetone by higher boiling butanone, and in this case, the reaction was finished after only 30 min, yielding 26a in the comparable yield of 41% (Procedure III, Table 3).
The alternative procedure with pre-dried CsF in DMF solution (Procedure IV) was also tested in reactions with **3a** and **3c**. After 3d at rt the reactions were finished and the $^1$H-NMR analysis of the crude mixtures indicated the presence of the expected 3H-1,2-dithioles **26a** and **26c**, which were isolated by column chromatography in 15% and 17% yields, respectively.

Notably, no formation of a corresponding 1,2,4-trithiolane was observed in any experiment performed with thiochalcones **3**.

A feasible reaction mechanism is presented in Scheme 10. The PPh$_3$ catalyzed sulfurization of thiochalcones involves $\alpha,\beta$-unsaturated thiocarbonyl S-sulfides **4** as plausible intermediates. They are formed via sulfur transfer from in situ-generated, neutral (and therefore less nucleophilic) triphenylphosphine polysulfides to the C=S group. In reactions catalyzed with CsF (Procedure IV), participation of fluoropolysulfide anion **8B** in the transfer of the sulfur atom is likely. In that case, however, the intermediate dithirane of type **21**, derived from the respective thiochalcone **3**, is believed to undergo ring opening along the C=S bond yielding the respective 1,3-dipole [22,23,28]. Thiocarbonyl S-sulfides derived from chalcones belong to the group of $\alpha,\beta$-unsaturated 1,3-dipoles and, therefore, they can undergo 1,5-electrocyclization [29] leading to the formation of 3H-1,2-dithioles, which apparently is a faster intramolecular process than the competitive [3+2]-cycloaddition with a ‘non-sulfurized’ molecule of the starting thiochalcone. Therefore, in none of the experiments formation of a respective 1,2,4-trithiolane was observed. Participation of thiocarbonyl S-sulfides in the [3+2]-cycloaddition with thiocarbonyl dipolarophiles is an important method for the synthesis of sulfur-rich heterocycles and diverse methods for the generation of this type of ‘sulfur-centered 1,3-dipoles’ are known [28]. Most importantly, the described 1,5-dipolar electrocyclization found for the first time in sulfurization reactions of thiochalcones offers a convenient method for the preparation of useful, five-membered 3H-1,2-dithioles **26**.

### 3. Materials and Methods

#### 3.1. Materials

Elemental sulfur (S$_8$) in the form of a powder (99.98% purity), molecular sieves 4Å (mesh 8–12), tetrabutylammonium fluoride (TBAF, 1.0 M solution in THF) and benzophenone (99%) were purchased from Merck (Sigma-Aldrich, Darmstadt, Germany). Triphenylphosphine (Ph$_3$P) (>95%), cesium fluoride (CsF) and 1,1,2,2-tetrachloroethane, used as internal standard in NMR analysis, were received from Tokyo Chemical Industry (TCI, Tokyo, Japan). Organic solvents were purchased from the following companies: tetrahydrofuran (99.9%) from Chemsolve (Witko, Lodz, Poland), dichloromethane (99.9%) from Honeywell (Charlotte, NC, USA), anhydrous N,N-dimethylformamide (99.8%) from Merck (Sigma-Aldrich), methanol (99.8%), acetone (99.5%) and petroleum ether 40/60 from Chempur (Piekary Śląskie, Poland). THF was dried over sodium (Na) with an addition of benzophenone, and acetone was distilled before its usage. Starting thiketones were obtained following reported procedures: thiobenzophenone (**1b**) from benzophenone by treatment with Lawesson’s reagent in toluene solution [18]; 2,2,4,4-tetramethylcyclobutane-1,3-dithione (‘dithione’) (**2a**), 2,2,4,4-tetramethyl-3-thioxocyclo-butanone (‘monothione’) (**2b**), and adamantanthione (**2c**) from 2,2,4,4-tetramethylcyclobutane-1,3-dione (**13**) and adamantane-2-one, respectively, by treatment with P$_4$S$_{10}$ in pyridine solution [18]. Thiochalcones **3** were prepared from the corresponding chalcones by thionation with Lawesson’s reagent and subsequently purified by column chromatography on silica gel [25,26].

#### 3.2. Analytical Methods and Equipment

The nuclear magnetic resonance (NMR) spectra were measured using a Bruker Avance III instrument (Bruker, Billerica, MA, USA) at 600 MHz ($^1$H-NMR) and at 151 MHz ($^{13}$C-NMR), respectively. Unless otherwise indicated the measurements were carried out in deuterochloroform (CDCl$_3$), using solvent signals as a reference ($^1$H-NMR, $\delta = 7.26$ ppm (CDCl$_3$); $^{13}$C-NMR, $\delta = 77.0$ ppm (CDCl$_3$)). Chemical shifts (\(\delta\)) were presented in ppm.
and coupling constants (J) were calculated in Hz. Integrals are given in accordance with assignments. Melting points were determined in capillaries with a Melt-Temp II apparatus (Laboratory Devices, Holliston, MA, USA). Elemental analyses were obtained with a Vario EL III instrument (Elementar Analysensysteme, Langenselbold, Germany).

3.3. Conversions of Thioketones 2a, 2b in the Presence of Fluoride Anion and Absence of S₈

3.3.1. Procedure I: TBAF/THF

To a stirred solution of pre-dried TBAF (0.1 mL of 1.0 M solution in THF) in 1.5 mL of dried THF, 0.5 mmol of the corresponding thioketone 2a or 2b was added at rt under Ar atmosphere. The solution was stirred and after ca. 5 min the color changed from rubin-red (2a) or orange-red (2b) to yellow-orange. Next, the solvent was evaporated in vacuo and the residue was pre-purified by filtration via a short chromatographic column filled with SiO₂ (ca. 2 cm layer). Crude mixtures were analyzed in the 1H-NMR spectra with weighted standard (Cl₂CH–CHCl₂). The products formed were identified by comparison of their spectroscopic data with reported ones. Yields reported below refer to the analysis of crude mixtures performed with weighted standard (method A) or to amounts of isolated products (method B).

3.3.2. Procedure II: CsF/DMF

In an alternative procedure, conversion of thioketone 2b was carried out in dry DMF (1.5 mL) using cat. amounts of freshly calcined cesium fluoride at rt under Ar atmosphere. After 2 h of magnetic stirring, the color still remained orange-red and no formation of other products was observed by TLC control. After that time, a drop of water was added to the stirred solution and the mixture rapidly changed the color to orange indicating thereby conversion of 2b. The reaction solution was diluted with a portion of CH₂Cl₂ (5 mL) and extracted four times with water (4 mL each). Collected organic fractions were dried over MgSO₄, filtered, and the solvent was evaporated. The mixture of crude products was analyzed in the 1H-NMR spectrum with weighted standard (Cl₂CH–CHCl₂); the yields of identified products 13, 15, and 16b were determined by method A.

3.3.3. Product Characterization

3,3-Dimethyl-4-(propan-2-ylidene)thietane-2-thione (14). Yield: Procedure I—92% (method A); 69 mg (80%) (method B). Yellow oil (ref. [18]). 1H-NMR: δ 1.47 (s, 2CH₃), 1.73 (s, CH₃), 1.86 (s, CH₃) ppm. 13C-NMR: δ 20.1 (CH₃), 21.9 (CH₃), 25.2 (2CH₃), 74.2 (C-3), 122.6 (=C), 131.0 (=C), 243.5 (C=S) ppm.

2′,2′,4′,4′-Tetramethyl-3′-oxocyclobutyl 2,2,4-trimethyl-3-oxopentanedithioate (15). Yield: Procedure I—59% (method A), 38 mg (48%) (method B); Procedure II—44% (method A). Yellow solid, m.p. 57–58 °C (ref. [18], m.p. 62–63 °C). 1H-NMR: δ 1.13 (d, J = 6.6 Hz, 2CH₃(CH)), 1.21 (s, 2CH₃), 1.47 (s, 2CH₃), 1.68 (s, 2CH₃), 2.91 (sept., J = 6.6 Hz, 2CH₃(CH)), 4.25 (s, =C-1′) ppm. 13C-NMR: δ 20.4 (2CH₃), 21.8 (2CH₃), 25.0 (2CH₃), 26.8 (2CH₃), 37.0 (C-4), 57.7 (C-2′, C-4′), 61.1, 69.4 (C-1′, C-2), 212.0 (C=O, C-3′), 218.9 (C=O, C-3, cyclobutanone), 241.2 (C=S) ppm. C₁₆H₂₆O₂S₂ (314.51): calculated, C 61.10, H 8.33, S 20.39; found, C 61.12, H 8.44, S 20.50.

3,3,5,5-Tetramethyl-2-thioxothiolan-4-one (16b). Yield: Procedure I—13% (method A); 9 mg (10%) (method B); Procedure II: 11% (method A). Yellow thick oil (ref. [4], mp 39–41 °C). 1H-NMR: δ 1.44 (s, 2CH₃), 1.70 (s, 2CH₃) ppm. 13C-NMR: δ 27.8, 28.1 (2CH₃ each), 61.3 (C-3), 63.4 (C-S), 216.7 (C=O), 234.1 (C=S) ppm.

2,2,4,4-Tetramethylycyclobutane-1,3-dione (13). Yield: Procedure I—12% (method A); Procedure II—8% (method A). 1H-NMR: δ 1.34 ppm. (ref. [30]).
3.4. General Procedures of the Fluoride Anion Catalyzed Sulfurization of Thioketones 1 and 2 with Elemental Sulfur (S\textsubscript{8})

3.4.1. Procedure I: TBAF/THF

To the suspension of elemental sulfur (calculated on atomic [S]) (0.25 mmol, Entry A; 0.50 mmol, Entry B; 1.00 mmol, Entry C, 2.00 mmol, Entry D, or 4.00 mmol, Entry E) in 1.5 mL of dry THF, under argon atmosphere, 0.1 mL (0.1 mmol, 20% mol. calculated on the amounts of thioketone used) of the tetrabutylammonium fluoride solution (TBAF, 1.0 M in THF), pre-dried over molecular sieves, was added dropwise. The mixture became homogenous. After ca. 10–15 min of magnetic stirring at rt, 0.5 mmol of the corresponding thioketone 1a or 2a,2c was added in small portions to the solution and stirring was continued for an appropriate time at rt (see Tables 1 and 2). Next, the solvent was evaporated in vacuum and the residue was pre-purified by filtration via a short chromatographic column filled with SiO\textsubscript{2} (ca. 2 cm layer). The crude mixtures were analyzed in the 1H-NMR spectra with weighted standard (Cl\textsubscript{4}CH\textsubscript{2}CH-CCH\textsubscript{2}) and subsequently separated on preparative chromatographic plates coated with silica gel. A mixture of petroleum ether and dichloromethane (in most cases the ratio of both solvents was 9:1 or 8:2) was used as an eluent. Yields refer either to analysis with weighted standard (method A) or to isolated amounts (method B).

3.4.2. Procedure II: CsF/DMF

In an alternative procedure reactions of thioketones 1a and 2a-c with 2.0 mmol of sulfur (Entry C') were carried out in dry DMF (2–3 mL) using catalytic amounts of freshly calcined cesium fluoride (CsF). After completion of the reactions, the mixture was diluted with dichloromethane and extracted several times with small portions of water to remove DMF. Following an alternative method for the removal of DMF, toluene (2–3 mL) was added in small portions and the solutions obtained thereby were warmed in a water bath (55 °C) to evaporate the solvents. Crude products were purified by column chromatography on silica gel using petroleum ether/dichloromethane mixtures as eluent.

3.4.3. Product Characterization

**Dispiro[adamantane-2,3'-1,2,4](trithiolane-5',2'″-adamantane] (5c).** Yields: Procedure I—(a) Entry A: 27 mg (59% based on S/30% based on 1c); (b) Procedure II—Entry C': 54 mg (59%) (method B). Colorless solid, m.p. 200–201 °C (methanol/CH\textsubscript{2}Cl\textsubscript{2}) (ref. [31], m.p. 191–192 °C). \textsuperscript{1}H-NMR: \(\delta\) 1.75–1.95 (m, 16H), 2.15–2.40 (m, 12H) ppm. \textsuperscript{13}C-NMR: \(\delta\) 36.7, 37.2, 37.9 (10CH each), 61.3 (C-1, C-3), 63.4 (C-8, C-10), 127.9, 128.5, 128.6 (20CH each) ppm. \textsuperscript{3}C-NMR: \(\delta\) 71.4 (C-3, C-6), 127.9, 128.5, 128.6 (20CH\textsubscript{arom}) ppm. \textsuperscript{15}C-NMR: \(\delta\) 71.4 (C-3, C-6), 127.9, 128.5, 128.6 (20CH\textsubscript{arom}), 141.7 (4C\textsubscript{arom}) ppm.

**3,3,6,6-Tetraphenyl-1,2,4,5-tetrathiane (6a).** Yields: Procedure I—(a) Entry B: 32 mg (28%) (method B); (b) Entry C: 60 mg (52%) (method B); (c) Procedure II—Entry C': 65 mg (56%) (method B). Colorless crystals, m.p. 210–212 °C (decomposition, blue) (methanol/CH\textsubscript{2}Cl\textsubscript{2}) (ref. [3], m.p. 209–209.5 °C). \textsuperscript{1}H-NMR: \(\delta\) 7.30–7.36 (m, 12CH\textsubscript{arom}), 7.55–7.59 (m, 8CH\textsubscript{arom}) ppm. \textsuperscript{13}C-NMR: \(\delta\) 71.4 (C-3, C-6), 127.9, 128.5, 128.6 (20CH\textsubscript{arom}) ppm. \textsuperscript{15}C-NMR: \(\delta\) 69.8 (C-3, C-6), 127.4, 128.2, 128.5 (20CH\textsubscript{arom}) ppm. \textsuperscript{16}C-NMR: \(\delta\) 141.7 (4C\textsubscript{arom}) ppm.

**1,1,3,3,8,10,10-Octamethyl-5,6,11,12-tetrathiadispiro-[3.2.3.3]dodecane-2,9-dione (6b).** Yields: Procedure I—(a) Entry A: 12% (method A); (b) Entry B: 40% (method A), 30 mg (32%) (method B). Colorless solid, m.p. 170–172 °C (methanol/CH\textsubscript{2}Cl\textsubscript{2}) (ref. [4], m.p. 169–170 °C). \textsuperscript{1}H-NMR: \(\delta\) 1.39 (s, br, 4CH\textsubscript{3}), 1.54 (s, br, 4CH\textsubscript{3}) ppm. \textsuperscript{13}C-NMR: \(\delta\) 20.9, 24.9 (4CH\textsubscript{3} each), 67.1 (C-1, C-3, C-8, C-10), 71.5 (C-4, C-7), 217.9 (C=O) ppm. \textsuperscript{16}C-NMR: \(\delta\) 141.7 (4C\textsubscript{arom}) ppm.

**1,1,3,3,8,10,10-Octamethyl-5,6,11,12-tetrathiadispiro-[3.2.3.3]-9-oxododecane-2-thione (6e).** Yield: Procedure I—(a) Entry B: 15 mg (15%) (method B). Orange oil. \textsuperscript{1}H-NMR: \(\delta\) 1.42 (s, br, 4CH\textsubscript{3}), 1.69 (s, br, 4CH\textsubscript{3}) ppm. \textsuperscript{13}C-NMR: \(\delta\) 27.8, 28.1 (4CH\textsubscript{3} each), 61.3 (C-1, C-3), 63.4 (C-8, C-10), 77.86, 77.91 (C-4, C-7), 216.6 (C=O) ppm. \textsuperscript{16}C-NMR: \(\delta\) 392.69: calculated, C 48.94, H 6.16, S 40.83; found, C 48.96, H 6.33, S 40.58.

**1,1,3,3,8,10,10-Octamethyl-5,6,11,12-pentathiadispiro-[3.2.3.3]-tridecane-2,9-dione (7a).** Yields: Procedure I—(a) Entry C: 35 mg (34%) (method B); (c) Entry D: 53 mg (52%) (method B); (d) Entry E: 61 mg (60%) (method B); Procedure II—(e) Entry C': 44 mg (43%) (method B).
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3.5. General Procedures for Sulfurization of Thiohalocanes 3 with Elemental Sulfur (S₈)

3.5.1. Procedure I: Ph₃P / Acetone

In a two-necked round-bottomed flask (10 mL) equipped with a magnetic stirrer, 0.5 mmol of the corresponding thiohalocane 3a–d, 0.125 mmol of elemental sulfur (S₈) was placed and 2 mL of dry acetone were added. The resulting mixture was heated to the reflux under condenser and under argon and stirred for the appropriate time (discoloring).
Then, the solvent was evaporated in vacuo and the residue was purified, firstly by short column chromatography and afterwards by thin-layer chromatography, by using SiO\textsubscript{2} as the absorbent and a mixture of petroleum ether and dichloromethane (9:1) as the eluent, yielding the corresponding 3H-1,2-dithiole derivative 26\textit{a}–d. Reported yields refer either to isolated amounts of products 26 (Method A) or to amounts calculated on the basis of standard analysis performed with weighted amounts of Cl\textsubscript{2}CH–CHCl\textsubscript{2} added to the crude mixture (method B).

3.5.2. Procedure II: PhSK/Acetone

In analogy to Procedure I, thiochalcone 3a was reacted with elemental sulfur in the presence of cat. amounts (0.06 mol-equiv.) of potassium thiophenolate (PhSK) in boiling acetone (see ref. [3,4]).

3.5.3. Procedure III: Ph\textsubscript{3}P/Butanone

In analogy to Procedure I, thiochalcone 3a was reacted with elemental sulfur in the presence of cat. amounts of PPh\textsubscript{3} using butanone as a solvent.

3.5.4. Procedure IV: CsF/DMF

Thiochalcones 3a or 3c, (1 mmol) and 64 mg (2.0 mmol) of sulfur were stirred magnetically in dry DMF (2.5 mL) with cat. amounts of freshly calcined cesium fluoride (CsF). After 72h the reaction solution was diluted with dichloromethane (25 mL) and extracted several times with small portions of water for removal of DMF. Combined organic layers were dried over MgSO\textsubscript{4}, filtered and purified by column chromatography on silica gel using a 95:5 mixture of petroleum ether and dichloromethane as eluent.

3.5.5. Product Characterization

3,5-Diphenyl-3H-1,2-dithiole (26a). Yields: (a) Procedure I—51 mg (40%) (method A), 63% (method B); (b) Procedure II—53 mg (41%) (method A); (c) Procedure III—19 mg (15%) (method A); Procedure IV: 38 mg (15%) (method A). Orange-red solid, m.p. 78–81\textdegree C. 1\textsuperscript{H}-NMR: δ 5.87 (d, J = 3.0 Hz, 1H, CH); 6.19 (d, J = 3.0 Hz, 1H, CH); 7.34–7.38 (m, 1H, CH\textsubscript{arom}); 7.39–7.44 (m, 5H, CH\textsubscript{arom}); 7.49–7.53 (m, 2H, CH\textsubscript{arom}); 7.57–7.61 (m, 2H, CH\textsubscript{arom}) ppm. 13\textsuperscript{C}-NMR: δ 63.7 (C-3); 120.7 (C-4); 127.4, 127.5, 128.4, 128.8, 129.0, 129.3 (10C\textsubscript{arom}); 132.9 (C-5); 140.8, 145.2 (2C\textsubscript{arom}) ppm. C\textsubscript{15}H\textsubscript{12}S\textsubscript{2} (256.39): calculated, C 70.27, H 4.72, S 25.01; found: C 70.20, H 4.68, S 25.01.

3-(4-Chlorophenyl)-5-phenyl-3H-1,2-dithiole (26b). Yield: (a) Procedure I—22 mg (15%) (method A). Red oil. 1\textsuperscript{H}-NMR: δ 5.80 (d, J = 3.6 Hz, 1H, CH); 6.15 (d, J = 3.6 Hz, 1H, CH); 7.36 (d, J = 9.0 Hz, 2H, CH\textsubscript{arom}); 7.39–7.45 (m, 4H, AB system), 7.39–7.42 (m, 5H, CH\textsubscript{arom}) ppm. 13\textsuperscript{C}-NMR: δ 62.7 (C-3); 120.1 (C-4); 127.4, 128.8, 129.1, 129.4 (9C\textsubscript{arom}); 132.7 (C-5); 134.2, 139.4, 145.7 (3C\textsubscript{arom}) ppm. C\textsubscript{15}H\textsubscript{11}S\textsubscript{2}Cl (290.83): calculated, C 61.95, H 3.81, S 22.05; found: C 61.68, H 3.85, S 22.01.

3-(4-Methylphenyl)-5-phenyl-3H-1,2-dithiole (26c). Yield: (a) Procedure I—27 mg (20%) (method A); Procedure IV—46 mg (17%) (method A). Red solid, m.p. 79–82 \textdegree C. 1\textsuperscript{H}-NMR: δ 2.39 (s, 3H, CH\textsubscript{3}); 5.86 (d, J = 3.3 Hz, 1H, CH); 6.18 (d, J = 3.3 Hz, 1H, CH); 7.21, 7.59 (2d, J = 8.4 Hz, 4H, AB system), 7.38–7.42 (m, 5H, CH\textsubscript{arom}) ppm. 13\textsuperscript{C}-NMR: δ 62.7 (C-3); 120.1 (C-4); 127.4, 128.8, 129.1, 129.4 (9C\textsubscript{arom}); 132.7 (C-5); 134.2, 139.4, 145.7 (3C\textsubscript{arom}) ppm. C\textsubscript{16}H\textsubscript{14}S\textsubscript{2} (270.41): calculated, C 71.07, H 5.22, S 23.72; found: C 70.92, H 5.43, S 23.61.

3-(4-Methoxyphenyl)-5-phenyl-3H-1,2-dithiole (26d). Yield: (a) Procedure I—17 mg (12%) (method A). Red oil. 1\textsuperscript{H}-NMR: δ 3.84 (s, 3H, OCH\textsubscript{3}); 5.87 (d, J = 3.6 Hz, 1H, CH); 6.17 (d, J = 3.6 Hz, 1H, CH); 6.93 (d, J = 9.0 Hz, 2H, CH\textsubscript{arom}); 7.38–7.44 (m, 5H, CH\textsubscript{arom}); 7.57–7.60 (m, 2H, CH\textsubscript{arom}) ppm. 13\textsuperscript{C}-NMR: δ 55.4 (OCH\textsubscript{3}), 63.3 (C-3), 114.3 (C-4), 121.0, 127.4, 127.7, 127.8, 129.21 (9C\textsubscript{arom}); 132.9 (C-5), 133.0, 144.8, 159.7 (3C\textsubscript{arom}) ppm.
4. Conclusions

The presented study showed that fluoride anion can be applied as an excellent activator of elemental sulfur in sulfurization reactions of easily available cycloaliphatic thio ketones derived from 2,2,4,4-tetramethylcyclobutane-1,3-dione. Depending on the molar ratio of the starting materials, sulfur-rich heterocycles with variable ring size can be obtained in satisfactory to good yields. In situ-generated fluoropolysulfide anions act as powerful sulfurizing reagents. As a key intermediate in the studied reactions, three-membered, reactive dithiiranes, formed via the addition of the latter to the C=S group, are postulated for both cycloaliphatic and aromatic thio ketones.

In contrast to thio ketones, their $\alpha,\beta$-unsaturated analogues, i.e., thiochalcones, do not undergo the sulfurization reaction with sulfur in the presence of fluoride anion. On the other hand, their sulfurization with elemental sulfur, leading to $3H$-1,2-dithiole derivatives, can be performed using triphenylphosphine ($PPh_3$) as a catalyst. The latter heterocycles are of interest as unique starting materials for the preparation of sulfur-heterocycles based on persistent radicals [32,33]. However, up to now, methods for the synthesis of $3H$-1,2- dithioles and their conversion into the stable organic radicals are rarely reported and they are described only in rather remote literature [34].

The developed protocols of sulfurization in the presence of fluoride anion can be of interest not only for the synthesis of sulfur-rich heterocycles, such as 1,2,4-trithiolanes [28], 1,2,4,5-tetrathianes [35,36] or 1,2,3,5,6-pentathiepanes, but also for the preparation of sulfur-rich polymers starting with alkyl- [37,38] or aryl [39] substituted thiranes. In the present work, fluoride anion was shown to act as an alternative, nucleophilic catalyst and can replace smelly and unstable sodium (or potassium) thiophenolate in the activation of elemental sulfur in reactions with thiranes. The presented research should be considered as a new contribution to our continuous studies on exploration of elemental sulfur and small-ring, congested $S$-heterocycles (thiaziridiens, thiranes) in sulfurization reactions of diverse organic compounds, including stable thio ketones [10,22,24,30] but also transient nucleophilic heterocyclic carbenes (NHC) [40,41].

Supplementary Materials: The Supplementary Materials are available online and they contain the scanned $^1$H- and $^{13}$C-NMR spectra for the described and isolated compounds. The re-determined X-ray crystallography data for compound 7a are deposited as CSD Communication under deposition number 2056867 (doi:10.5517/ccdc.csd.ccs271bk6).

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Sample Availability: Samples of the compounds 5a, 6a,b,e, 7a-7c, 13-15, 16a-16b, meso-17, d,l-17, 19, and 26a-26d are available from the authors.

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