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## On the mechanism of formation of 1,4,5,8-tetrathianaphthalene (TTN) from dimercaptoisotrithione (dmit) derivatives<sup>†</sup>

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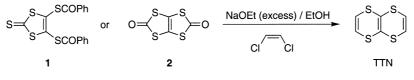
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## Abstract

The mechanism of formation of TTN (an important precursor to tetrathiafulvalene (TTF)) from 4,5bis(benzoylthio)-1,3-dithiole-2-thione is discussed. Contrary to previous reports, ethylenetetrathiolate is not an intermediate in this synthesis, whereas 4,5-vinylenedithio-1,3-dithiole-2-thione is likely to be. The latter is prepared by a new synthesis and converted into TTN in one step. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Diels-Alder reactions; dithioles; sulfoxides; sulfur heterocycles.

1,4,5,8-Tetrathianaphthalene (TTN), first prepared by Cava and co-workers,<sup>1</sup> is a compound of current interest since its isomerization in a basic medium is reported to afford tetrathiafulvalene (TTF) in very good yield.<sup>2–7</sup> Most syntheses of TTN start from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione  $1,^{3,5-8}$  although the use of thiapendione 2 has occasionally been reported<sup>3,7</sup> (Scheme 1). In order to explain the formation of TTN in these reactions, ethylenetetrathiolate 3 is supposed to be generated, presumably by attack of excess sodium ethoxide on the initially formed disodium salt of dmit 4 (Scheme 2). Nevertheless, the existence of 3 has been challenged recently,<sup>9,10</sup> at least in reactions which make use of thiapendione as starting material.



Scheme 1.

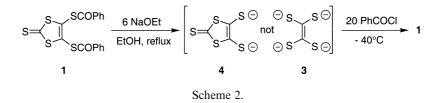
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<sup>&</sup>lt;sup>†</sup> Dedicated to Professor José Barluenga on the occasion of his 60th anniversary.

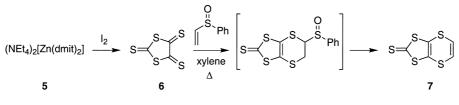
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In this communication we report that, despite previous reports, ethylenetetrathiolate **3** is not an intermediate in the synthesis of TTN from **1** and suggest an alternative mechanism for this reaction.

Treatment of **1** with six equivalents of NaOEt in refluxing EtOH (4 hours), followed by reaction with an excess (20 equivalents) of benzoyl chloride did not give the expected tetrakis(benzoylthio)-ethylene. Instead, compound **1** was obtained in 60% yield (Scheme 2).<sup>‡</sup> This observation points to the fact that dianion **4**, which is generated quantitatively in the basic medium after a few minutes at room temperature,<sup>15</sup> reacts stepwise. It is likely that 4,5-vinylenedithio-1,3-dithiole-2-thione (7) is first formed from **4** and 1,2-dichloroethylene by a sequence of elimination and addition steps, as first demonstrated by Truce on his papers on nucleophilic substitutions of vinyl halides by thiols.<sup>16,17</sup> The fact that compound **7** is obtained in low yield from **4** and 1,2-dibromoethylene<sup>18</sup> must not be taken as evidence supporting the intermediacy of **3** in the present case,<sup>6</sup> since the reaction in Ref. 18 was carried out in the absence of NaOEt, what precludes the same kind of mechanism and points to an alternative addition–elimination sequence.<sup>19,20</sup>



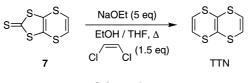
To test this hypothesis, we decided to prepare 7. Although the reported syntheses of this compound rely on the final elimination of EtOH from ethoxyethylenedithio-1,3-dithiole-2-thione,<sup>21,22</sup> we found a new, experimentally simpler method, which makes use of phenyl vinyl sulfoxide, a synthetic equivalent of acetylene in Diels–Alder cycloadditions.<sup>23</sup> Thus, reaction of trithione  $6^{12}$  with phenyl vinyl sulfoxide in refluxing xylene afforded 7 in one step in 50% yield (Scheme 3).



Scheme 3.

Finally, reaction of 7 with NaOEt (5 equivalents) and cis-1,2-dichloroethylene (1.5 equivalents) led to TTN in 85% yield (Scheme 4). It is noteworthy that this new synthesis of TTN is similar to that originally reported by Cava<sup>1</sup> but the reactants are at the right oxidation level, thus eliminating the extra oxidation step.

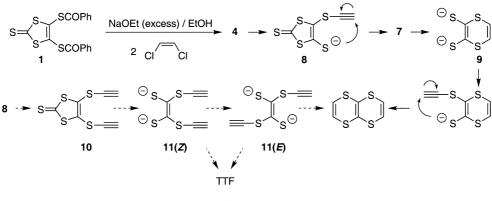
<sup>&</sup>lt;sup>‡</sup> The analogous reaction with AcCl at  $-80^{\circ}$ C gave a complex mixture in which 4,5-bis(acetylthio)-1,3-dithiole-2thione<sup>11</sup> and a compound of formula C<sub>6</sub>S<sub>8</sub> (HRMS, M+· (m/z = 327.7764), calcd: 327.7766) were identified. Although the exact structure of the latter is not known, its formation can be related to reactions of dmit with very reactive halides, giving rise to oxidation products.<sup>12</sup> Moreover, two different structures have been proposed for C<sub>6</sub>S<sub>8</sub> isomers formed from oxidation reactions of dmit derivatives.<sup>13,14</sup>



Scheme 4.

These observations demonstrate that tetraanion **3** is not an intermediate in the synthesis of TTN from **1**, as is often stated. On the other hand, **7** can be formed under the reaction conditions and rapidly cleaved by additional base to dianion  $9^{24}$  which explains that **7** cannot be isolated from the reaction of **1** with 1,2-dichloroethylene in the presence of excess NaOEt. A possible mechanism for the conversion of **1** to TTN which accounts for the experimental facts is depicted in Scheme 5: the ethynylthio group in **8** results from addition of one thiolate group of **4** to chloroacetylene followed by *anti* elimination; subsequent intramolecular addition of the remaining thiolate affords **7** and eventually, by a similar sequence starting from **9**, TTN. An alternative mechanism involving intermediates **10** and **11** (dashed arrows in Scheme 5) can be ruled out for the following reasons:

- (i) Intramolecular cyclization of **8** is likely to proceed faster than intermolecular attack to chloroacetylene to afford **10**.
- (ii) Even if 10 is formed, dithiole ring-opening would afford salt 11(Z) which can only cyclize to TTF (not to TTN), contrary to observations.
- (iii) Possible isomerization of 11(Z) to 11(E), which could give rise to TTN, is unlikely since it is generally believed that 11(E) is the intermediate in the conversion of TTN to TTF<sup>2,6</sup> and it is well known that (Z)-1,2-bis(alkylthio)ethylene-1,2-dithiolates are configurationally stable.<sup>25</sup>



Scheme 5.

To summarize, we have demonstrated that ethylenetetrathiolate **3** is not formed by basic cleavage of **1**. On the other hand, compound **7** has been converted into TTN and seems a likely intermediate in the synthesis of the latter from **1**. A possible mechanism for the overall sequence  $1 \rightarrow \text{TTN}$  which explains all experimental facts is proposed.

## Acknowledgements

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