



On the mechanism of formation of 1,4,5,8-tetrathianaphthalene (TTN) from dimercaptoisotrithione (dmit) derivatives[†]

Raquel Andreu, Javier Garín,* Jesús Orduna and José M. Royo

Departamento de Química Orgánica, ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

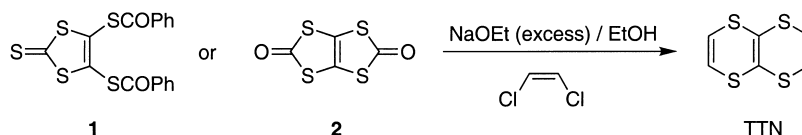
Received 14 April 2000; accepted 19 May 2000

Abstract

The mechanism of formation of TTN (an important precursor to tetrathiafulvalene (TTF)) from 4,5-bis(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,¹ is a compound of current interest since its isomerization in a basic medium is reported to afford tetrathiafulvalene (TTF) in very good yield.^{2–7} 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^{3,7} (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,^{9,10} at least in reactions which make use of thiapendione as starting material.



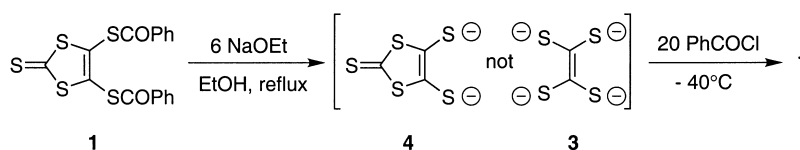
Scheme 1.

* Corresponding author. Fax: +34-976-761194; e-mail: jgarin@posta.unizar.es

[†] Dedicated to Professor José Barluenga on the occasion of his 60th anniversary.

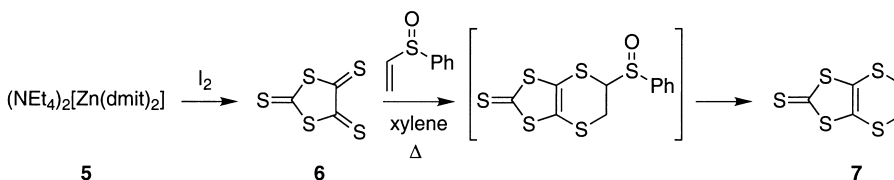
In this communication we report that, despite previous reports, ethylenetetrathiolate **3** is not an intermediate in the synthesis of TTN from **1** and suggest an alternative mechanism for this reaction.

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).[‡] This observation points to the fact that dianion **4**, which is generated quantitatively in the basic medium after a few minutes at room temperature,¹⁵ 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.^{16,17} The fact that compound **7** is obtained in low yield from **4** and 1,2-dibromoethylene¹⁸ must not be taken as evidence supporting the intermediacy of **3** in the present case,⁶ 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.^{19,20}



Scheme 2.

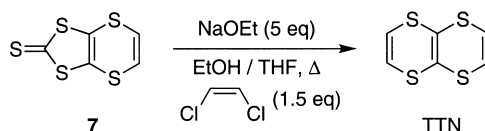
To test this hypothesis, we decided to prepare **7**. Although the reported syntheses of this compound rely on the final elimination of EtOH from ethoxyethylenedithio-1,3-dithiole-2-thione,^{21,22} we found a new, experimentally simpler method, which makes use of phenyl vinyl sulfoxide, a synthetic equivalent of acetylene in Diels–Alder cycloadditions.²³ 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 Cava¹ but the reactants are at the right oxidation level, thus eliminating the extra oxidation step.

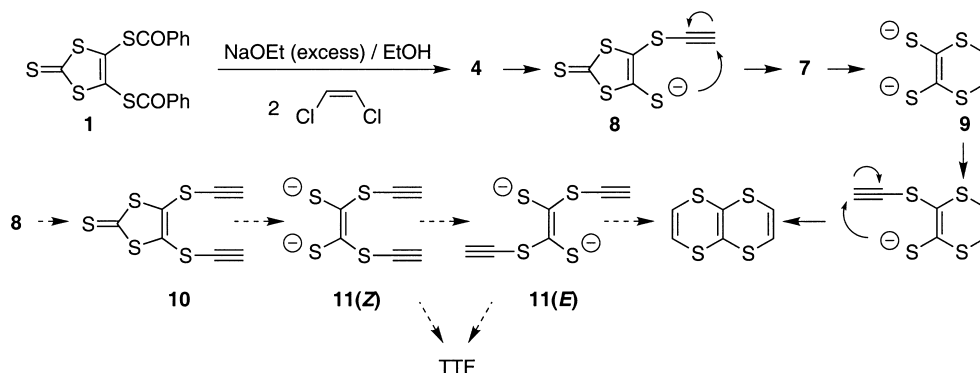
[‡] The analogous reaction with AcCl at -80°C gave a complex mixture in which 4,5-bis(acetylthio)-1,3-dithiole-2-thione¹¹ and a compound of formula C₆S₈ (HRMS, M⁺ (*m/z* = 327.7764), calcd: 327.7766) were identified. Although the exact structure of the latter is not known, its formation can be related to reactions of dmit with very reactive halides, giving rise to oxidation products.¹² Moreover, two different structures have been proposed for C₆S₈ isomers formed from oxidation reactions of dmit derivatives.^{13,14}



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:

- Intramolecular cyclization of **8** is likely to proceed faster than intermolecular attack to chloroacetylene to afford **10**.
- 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.
- 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^{2,6} and it is well known that (*Z*)-1,2-bis(alkylthio)ethylene-1,2-dithiolates are configurationally stable.²⁵



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**→TTN which explains all experimental facts is proposed.

Acknowledgements

Financial support from DGESIC (MAT1999-1009-C02-02) is gratefully acknowledged.

References

1. Mizuno, M.; Cava, M. P.; Garito, A. F. *J. Org. Chem.* **1976**, *41*, 1484–1485.
2. Nakatsuji, S.; Amano, Y.; Kawamura, H.; Anzai, H. *J. Chem. Soc., Chem. Commun.* **1994**, 841–842.
3. Meline, R. L.; Elsenbaumer, R. L. *Synth. Met.* **1997**, *86*, 1845–1846.
4. Nakatsuji, S.; Amano, Y.; Kawamura, H.; Anzai, H. *Liebigs Ann./Recueil* **1997**, 729–732.
5. Meline, R. L.; Elsenbaumer, R. L. *Synthesis* **1997**, 617–619.
6. Meline, R. L.; Elsenbaumer, R. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2467–2469.
7. Meline, R. L.; Elsenbaumer, R. L. *Synth. Met.* **1999**, *102*, 1658–1661.
8. Varma, K. S.; Sasaki, N.; Clark, R. A.; Underhill, A. E.; Simonsen, O.; Becher, J.; Bøwadt, S. *J. Heterocyclic Chem.* **1988**, *25*, 783–787.
9. Keefer, C. E.; Purrington, S. T.; Bereman, R. D. *Synthesis* **1998**, 1710–1712.
10. Keefer, C. E.; Purrington, S. T.; Bereman, R. D.; Knight, B. W.; Bedgood Jr., D. R.; Boyle, P. D. *Inorg. Chim. Acta* **1998**, *282*, 200–208, and references cited therein.
11. Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49–55.
12. Svenstrup, N.; Becher, J. *Synthesis* **1995**, 215–235, and references cited therein.
13. Ushijima, H.; Sudoh, S.; Kajitani, M.; Shimizu, K.; Akiyama, T.; Sugimori, A. *Inorg. Chim. Acta* **1990**, *175*, 11–12.
14. Chou, J.-H.; Rauchfuss, T. B.; Szczepura, L. F. *J. Am. Chem. Soc.* **1998**, *120*, 1805–1811, and references cited therein.
15. Varma, K. S.; Bury, A.; Harris, N. J.; Underhill, A. E. *Synthesis* **1987**, 837–838.
16. Truce, W. E.; Boudakian, M. M.; Heine, R. F.; McManimie, R. J. *J. Am. Chem. Soc.* **1956**, *78*, 2743–2748.
17. Truce, W. E.; Kassinger, R. *J. Am. Chem. Soc.* **1958**, *80*, 1916–1919, and references cited therein.
18. Varma, K. S.; Underhill, A. E. *Physica* **1986**, *143B*, 321–323.
19. Truce, W. E.; Kassinger, R. *J. Am. Chem. Soc.* **1958**, *80*, 6450–6453.
20. Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *J. Org. Chem.* **1983**, *48*, 4795–4800.
21. Yamada, J.; Satoki, S.; Anzai, H.; Hagiya, K.; Tamura, M.; Nishio, Y.; Kajita, K.; Watanabe, E.; Konno, M.; Sato, T.; Nishikawa, H.; Kikuchi, K. *Chem. Commun.* **1996**, 1955–1956, and references cited therein.
22. Yamochi, H.; Saito, G. *Synth. Met.* **1997**, *85*, 1467–1468.
23. Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597–1599.
24. Nakamura, T.; Nogami, T.; Shirota, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3447–3449.
25. Köster, J.; Hartke, K. *Arch. Pharm. (Weinheim)* **1984**, *317*, 995–1002.