

# A high yield conversion of tetrathiafulvalene into bis(ethylenedithio)tetrathiafulvalene and derivatives

Ronald L. Meline and Ronald L. Elsenbaumer \*<sup>†</sup>

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, USA

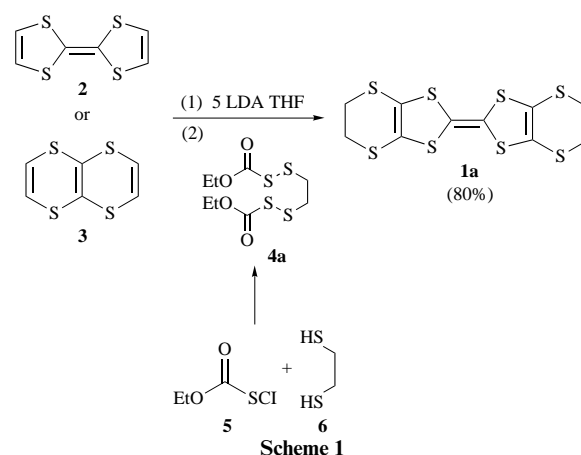
TTF is converted into BEDT-TTF (80%) in a one pot reaction.

BEDT-TTF **1a** has been utilized as the donor in the bulk of known superconducting organic molecular solids.<sup>1,2</sup> Although commercially available, BEDT-TTF is invariably expensive and thus a number of synthetic routes to the donor have been reported.<sup>3-6</sup> Literature syntheses most commonly involve the multistep formation of 4,5-ethylenedithio-1,3-dithiol-2-one, which is then coupled by trialkyl phosphite. Recently, we have reported a modest yield synthesis of BEDT-TTF circumventing this coupling step.<sup>7</sup>

In addition to thiones and ketones based on dimercaptioisotriothione (DMIT, 1,3-dithiole-2-thioxo-4,5-dithiolate), TTF **2** has been used extensively in recent years as the building block for extended donors owing to the acidity of its vinylic protons as first reported by Green, who demonstrated the proton-lithium exchange by treatment of TTF with Bu<sup>n</sup>Li or LDA.<sup>8</sup> Tetrakis(alkylchalcogeno)TTFs have been synthesized by utilizing tetralithiated TTF with subsequent elemental selenium or tellurium insertion into the carbon-lithium bond pairs, or with the use of disulfide electrophiles.<sup>9-12</sup> It should be noted that insertion of elemental sulfur into the carbon-lithium bond has been reported as difficult<sup>13</sup> or essentially non-existent.<sup>10</sup> Attempted alkylative ring closure of tetrakis(chalcogeno)TTF tetraanions with dibromoalkanes leads to polymeric products (*i.e.* intermolecular alkylation) even under high dilution conditions.<sup>9,14</sup> Chalcogen analogues based on BEDT-TTF (*i.e.* capped donors, BEDSe-TTF, BEDTe-TTF) have been prepared by Lee and Williams from TTF through the use of protecting group chemistry and solvent manipulation, respectively.<sup>14,15</sup> As a result of the difficulty of sulfur insertion and subsequent intramolecular alkylation with 1,2-dibromoethane, a facile conversion of TTF into BEDT-TTF has not been realized.

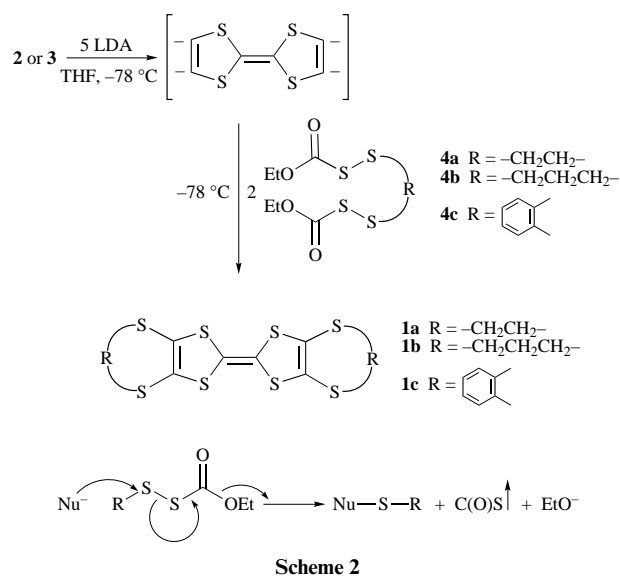
Building on prior synthetic routes to alkylthioTTFs from disulfides, a novel bisdisulfide was synthesized incorporating an ethyl spacing unit and ester leaving groups. Upon nucleophilic attack of tetralithiated TTF or isomerized tetralithiated tetrathianaphthalene (TTN, **3**) onto 1,2-bis(ethoxycarbonyldithio)ethane **4a**, BEDT-TTF was produced along with four equivalents of ethanol and four equivalents of carbon oxysulfide. The simple by-products facilitated workup, realizing BEDT-TTF in an overall yield of 80% from TTF.

The bisdisulfide **4a** was synthesized from two equivalents of ethoxycarbonylsulfonyl chloride<sup>16</sup> **5** and one equivalent of ethane-1,2-dithiol **6** in quantitative yield. Crystalline **4a** is completely soluble in THF or diethyl ether. Disulfide formation is based on the chemistry of Brois, who has utilized alkoxy-carbonylsulfonyl chlorides and a variety of thiols to produce ester alkyl disulfides [EtOC(O)S-S'R] which selectively yield unsymmetrical disulfides (R'-S-S-R'') upon reaction with one



equivalent of a different thiol (R''SH).<sup>16</sup> In this study, the carbanions of tetralithiated TTF easily add ethanedithiol units from **4a** producing BEDT-TTF.

The overall utility of this approach can be seen in light of recent reports of new facile syntheses and even bulk syntheses of TTF.<sup>7,17</sup> The alkoxy-carbonylsulfonyl chloride can be used to prepare a number of alkyl (**4a**, **4b**) and aryl (**4c**) spaced bisdisulfides from various dithioles leading to a series of capped TTFs (**1a**, **1b**, **1c**), thereby demonstrating the general utility of this approach.



## Experimental

### 1,2-Bis(ethoxycarbonyldithio)ethane **4a**

Ethoxycarbonylsulfonyl chloride **5** was prepared in very high yield according to a published procedure.<sup>18</sup> 12.00 g (85 mmol) of **5** was dissolved in 100 ml of dichloromethane, placed in a

<sup>†</sup> E-Mail: elsenbaumer@uta.edu

250 ml round bottomed flask capped with a septum, and cooled with a dry ice-isopropyl alcohol bath to  $\sim -30^\circ\text{C}$  under  $\text{N}_2$ . 4.00 g (42.5 mmol) **6** dissolved in 20 ml of dichloromethane was syringed into the flask over a 10 min period turning the yellow solution colorless. The solution was washed with 5% aq. NaOH, water and dried with  $\text{MgSO}_4$ . The filtered solution was condensed to give an oil which crystallizes on standing. Yield 12.68 g (98.7%); mp  $44-45^\circ\text{C}$ ;  $\delta_{\text{H}}(\text{CDCl}_3\text{-SiMe}_4)$  1.35 (t, 6H), 3.07 (s, 4H), 4.36 (q, 4H);  $\delta_{\text{C}}(\text{CDCl}_3\text{-SiMe}_4)$  14.1, 37.5, 65.2, 168.8;  $m/z$  (EI) 302 ( $\text{M}^+$ ).

#### 1,2-Bis(ethoxycarbonyldithio)propane **4b**

Same procedure as **4a** producing a yellow liquid. Yield 97.0%;  $\delta_{\text{H}}(\text{CDCl}_3\text{-SiMe}_4)$  1.34 (t, 6H), 2.06 (quintet, 2H), 2.93 (t, 4H), 4.35 (q, 4H);  $\delta_{\text{C}}(\text{CDCl}_3\text{-SiMe}_4)$  14.1, 26.9, 36.8, 65.0, 169.0;  $m/z$  (EI) 316 ( $\text{M}^+$ ).

#### 1,2-Bis(ethoxycarbonyldithio)benzene **4c**

Same procedure as **4a** producing crystals. Yield 94.2%; mp  $49-51^\circ\text{C}$ ;  $\delta_{\text{H}}(\text{CDCl}_3\text{-SiMe}_4)$  1.34 (t, 6H), 4.35 (q, 4H), 7.30 (m, 2H), 7.67 (m, 2H);  $\delta_{\text{C}}(\text{CDCl}_3\text{-SiMe}_4)$  14.2, 65.5, 129.0, 131.0, 136.5, 168.1;  $m/z$  (EI) 350 ( $\text{M}^+$ ).

#### BEDT-TTF **1a**

$\text{Bu}^{\text{t}}\text{Li}$  (40 ml of a 2.5 M solution in hexanes, 100 mmol) was syringed through a rubber septum into a solution of diisopropylamine (15 ml, 107 mmol) in dry THF (50 ml) in a 500 ml round bottomed flask with a stirrer bar at  $-78^\circ\text{C}$  (dry ice/isopropyl alcohol) under nitrogen (purge through rubber septum) to form lithium diisopropylamide (LDA). After stirring the solution for 1 h, TTF or TTN (**6**) (4 g, 19.6 mmol) was dissolved in dry THF (200 ml) and added to a pressure equalizing funnel and placed on top of the flask. Nitrogen was then transferred to the top of the funnel. The TTF solution was then added dropwise over a 4 h period to the LDA solution giving a bright yellow solution. The solution was stirred for an additional 4 h whereupon the funnel was then charged with 12.68 g of **4a** (42 mmol) dissolved in 80 ml of THF. The bisdisulfide solution was added over a 2 h period, and the reaction flask was allowed to warm to room temperature overnight. The resulting red suspension was filtered on a glass sintered funnel, washed with water (100 ml), methanol (100 ml) and finally diethyl ether (200 ml) to give pure BEDT-TTF 6.03 g [mp  $244-247^\circ\text{C}$  (decomp.)], in powder form. BEDT-TTF can be recrystallized from  $\text{CS}_2$ , sulfolane or thiophene.<sup>7</sup> Similar reaction procedures were used to prepare **1b** [yield 68%, mp  $246-250^\circ\text{C}$  (decomp.)],

lit.,<sup>19</sup> mp  $>250^\circ\text{C}$  (decomp.)] and **1c** [yield 72%, mp  $284-287^\circ\text{C}$  (decomp.)], lit.,<sup>20</sup> mp  $286-287^\circ\text{C}$  (decomp.)] which are identical to the known organic metals.<sup>19-22</sup>

### Acknowledgements

The authors would like to thank AFOSR for financial support as well as C. M. Land and V. V. Sorokin for technical assistance.

### References

- 1 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and H. Whangbo, *Organic Superconductors*, Prentice Hall, New Jersey, 1992.
- 2 H. Mori, *Int. J. Mod. Phys. B*, 1994, **8**, 1.
- 3 J. Larsen and C. Lenoir, *Synthesis*, 1989, 134.
- 4 J. Larsen and C. Lenoir, *Org. Synth.*, 1995, **72**, 265.
- 5 H. Müller and Y. Ueba, *Synthesis*, 1993, 853.
- 6 N. Svenstrup, K. M. Rasmussen, T. K. Hansen and J. Becher, *Synthesis*, 1994, 809.
- 7 R. L. Meline and R. L. Elsenbaumer, *Synthesis*, 1997, **6**, 617.
- 8 D. C. Green, *J. Org. Chem.*, 1979, **44**, 1476.
- 9 E. Aharon-Shalom, J. Y. Becker, J. Bernstein, S. Bittner and S. Shaik, *Tetrahedron Lett.*, 1985, 2783.
- 10 S. Hsu and L. Y. Chiang, *J. Org. Chem.*, 1987, **52**, 3444.
- 11 N. Okada, H. Yamochi, F. Shinozaki, K. Oshima and G. Saito, *Chem. Lett.*, 1986, 1861.
- 12 H. Yamochi, N. Iwasawa, H. Urayama and G. Saito, *Chem. Lett.*, 1987, 2265.
- 13 M. R. Bryce, personal communication.
- 14 V. Y. Lee, *Synth. Met.*, 1987, **20**, 161.
- 15 A. M. Kini, B. D. Gates, M. A. Beno and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1989, 169.
- 16 S. J. Brois, J. F. Pilot and H. W. Barnum, *J. Am. Chem. Soc.*, 1970, **92**, 7629.
- 17 A. J. Moore and M. R. Bryce, *Synthesis*, 1997, **4**, 407.
- 18 G. Barany, A. L. Schroll, A. W. Mott and D. A. Halsrud, *J. Org. Chem.*, 1983, **48**, 4750.
- 19 M. Mizuno, A. F. Garito and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1978, 18.
- 20 H. Müller, H. P. Fritz, R. Nemetshek, R. Hackl, W. Biberacher and C. P. Heidmann, *Z. Naturforsch., B*, 1992, **47**, 718.
- 21 L. C. Porter, A. M. Kini and J. M. Williams, *Acta Crystallogr.*, 1987, **C43**, 998.
- 22 J. P. Parakka, A. M. Kini and J. M. Williams, *Tetrahedron Lett.*, 1996, 8085.

Paper 7/07814E

Received 22nd October 1997

Accepted 23rd October 1997