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A Straightforward Approach to the Synthesis of Unsymmetrical Tetrathioalkyl Tetrathiafulvalene Derivatives

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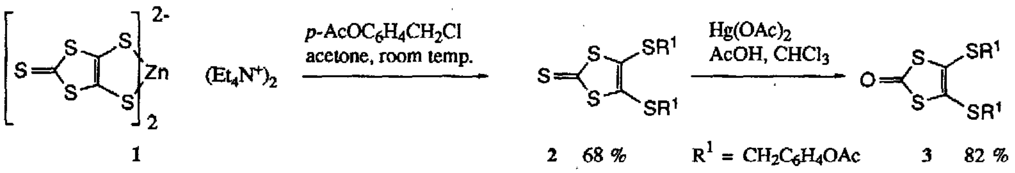
Abstract - The *p*-acetoxybenzylthio protecting group has been found to be compatible with the triethylphosphite mediated cross-coupling of 4,5-dialkylthio-1,3-dithiol-2-ones, providing access to the tetrathiolate **5**, and to dithiolates **11a** and **11b**, which are excellent precursors for unsymmetrical tetrathioalkyl tetrathiafulvalene derivatives.

Symmetrical tetrathiafulvalene (TTF) derivatives have been intensely investigated in recent years because of their ability to form charge transfer compounds, and their potential as molecular conductors and superconductors.[2] For the synthesis of novel electroactive materials, attention is now being focussed increasingly on unsymmetrical TTF's, and on the incorporation of TTF's into more complex molecular architectures . In our own work we have been concerned with the introduction of TTF moieties into metal binding macrocycles.[3] However, the synthesis of unsymmetrical TTF's is complicated by the lack of general routes to such compounds.[4] We have therefore been seeking a route to dithiolates, such as **11**, (Scheme 3) which would provide an excellent precursor to a variety of unsymmetrical TTF derivatives as well as a direct entry into TTF containing macrocycles. In this paper we report the successful synthesis of dithiolates **11a** and **11b**.

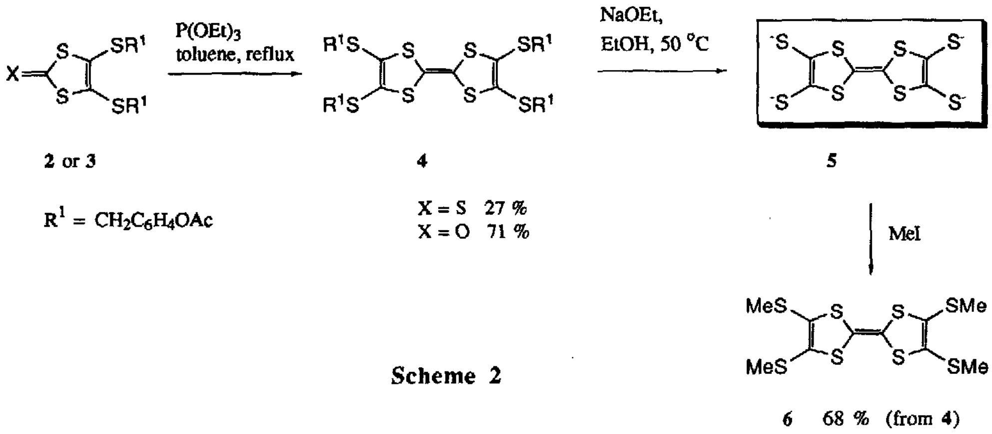
An obvious route to dithiolates, such as **11**, would involve the cross coupling of a 1,3-dithiol-2-one with a suitably bisprotected 4,5-dithiole-1,3-dithiol-2-one.[5] Unfortunately the more conventional protecting groups, such as benzoyl or acetyl, are incompatible with most of the cross-coupling methods available. We therefore decided to use the *p*-acetoxybenzyl protecting group[6] in the hope that this would be stable during cross-coupling, but could still be removed, under mild and basic conditions, to generate the desired dithiolate.

The bis acetoxybenzyl protected 4,5-dithiole-1,3-dithiol-2-thione **2** is readily synthesised by direct reaction of *p*-acetoxybenzyl chloride with the zinc complex **1** (Scheme 1), which can be prepared on a large scale by the sodium metal reduction of carbon disulphide in the presence of N,N-dimethylformamide.[7] Thione **2** can then be transformed into the corresponding protected 4,5-dithiole-1,3-dithiol-2-one **3** using mercuric acetate.[8]



Scheme 1

Treatment of the thione **2** with 4 equiv. of triethylphosphite in toluene, at reflux, gave the symmetrical tetra *p*-acetoxybenzylthiol TTF **4** in a modest 27 % yield, but identical reaction of **3** with triethyl phosphite, gave the same TTF **4** in an excellent 71 % yield, after recrystallisation from toluene/hexane (Scheme 2).

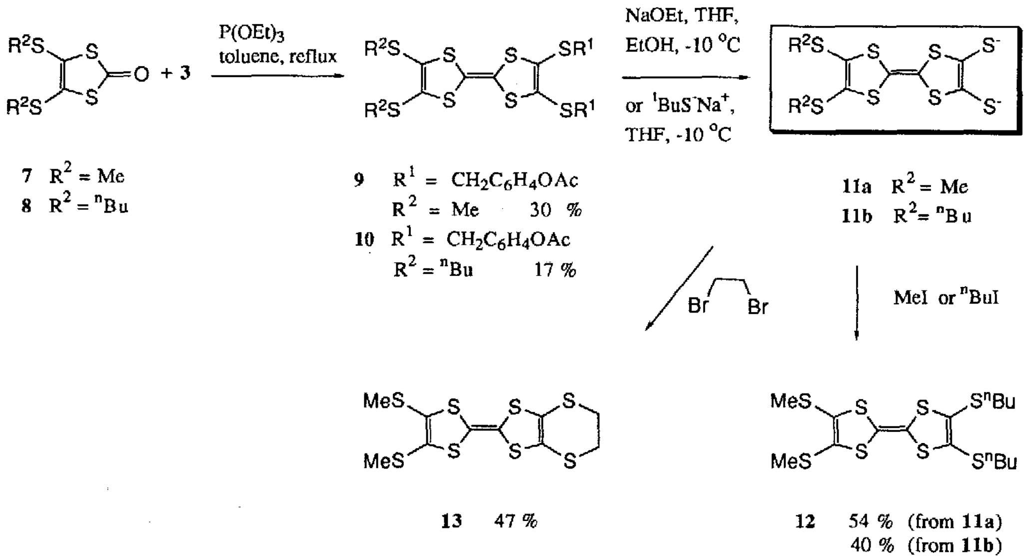


Scheme 2

These results contrast with the reported <1 % yield for the phosphite mediated coupling of the benzoyl protected 4,5-dithiole-1,3-dithiol-2-thione (**2**, R^1 = COPh)[9] and is also an improvement on the recently reported dicobalt octacarbonyl coupling of the same thione which proceeds in 25 % yield.[10] Treatment of a suspension of the tetraprotected TTF **4** in EtOH with 4 equiv. of NaOEt, and warming to 50 °C gave a dark red solution of the tetrathiolate anion, which was trapped with methyl iodide, to give the known[11] tetramethylthio TTF **6** in 68 % yield (Scheme 2). The tetrathiolate anion can also be trapped with 1,2 dibromoethane to yield bis(ethylenedithio)tetrathiofulvalene (BEDT-TTF).[10] The use of the *p*-acetoxybenzyl protecting group therefore provides a new and extremely convenient route to symmetrical tetraalkylthioTTF derivatives.

To prepare unsymmetrical TTF derivatives we investigated the phosphite mediated cross-coupling of the diprotected oxone **3** with 4,5-dimethylthio-1,3-dithiol-2-one **7** and with 4,5-dibutylthio-1,3-dithiol-2-one

8 (Scheme 3). Reaction of an equimolar quantity of **3** and **7** in refluxing toluene with triethyl phosphite (4 equiv.) gave a mixture of tetraprotected TTF **4** (28 %), the tetramethylthio TTF **6** (26 %) and the desired unsymmetrical TTF **9** (30 %). These three compounds could be conveniently separated by flash column chromatography and isolated, analytically pure, after recrystallisation.[12] The corresponding unoptimised cross-coupling of **3** with **8** gave **4** (15 %), the tetrabutylthio TTF (24%) and the unsymmetrical TTF **10** (17 %).[12]



Scheme 3

To remove the protecting groups, and generate dithiolate **11a** for further reaction, we first tried treating a suspension of **9** in ethanol with two equivalents of sodium ethoxide, in ethanol, and warming to 50 °C. The development of a red solution suggested that the desired dithiolate was indeed forming, but addition of methyl iodide or butyl iodide to this solution led to only low yields of the corresponding tetraalkylthio TTF's. However, addition of sodium ethoxide solution in ethanol, or of sodium *tert*-butylthiolate in tetrahydrofuran, to a solution of **9** or **10** in tetrahydrofuran, at -10 °C, again gave rise to a deep red solution of the dithiolate anion, which on quenching with methyl iodide or butyl iodide gave the desired unsymmetrical TTF **12** in much improved yields of 54 % (from **9**) and 40 % (from **10**). Dithiolate **11a** was also successfully trapped with 1,2 dibromoethane to give the known[13] cyclic TTF derivative **13** in 47% yield.

In conclusion, we have developed a convenient route to the dithiolates **11a** and **11b**, and to the tetrathiolate **5**, which should prove to be useful synthons in the synthesis of TTF derivatives. Further work on the use of these synthons in the preparation of larger TTF containing macrocycles, and novel electroactive molecules, is in progress and will be reported in due course.

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12. Data for **9**: m.p. 80 - 85 °C, δH ($CDCl_3$) 7.27 (4 H, d, 8 Hz), 7.05 (4 H, d, 8 Hz), 3.90 (4 H, s), 2.50 (6 H, s), 2.30 (6 H, s); m/z 656. Found C, 47.07; H, 3.70. $C_{26}H_{24}O_4S_8$ requires C, 47.56; H, 3.65. Data for **10**: m.p. 90 - 92 °C, δH ($CDCl_3$) 7.31 (4 H, d, 8 Hz), 7.05 (4 H, d, 8 Hz), 3.90 (4 H, s), 2.87 (4 H, t, 7 Hz), 2.30 (6 H, s), 1.80 - 1.20 (8 H, m), 0.98 (6 H, t, 7 Hz); m/z 740.
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