A Facile Preparation of Tetrathiafulvalenes having Alkylthio Groups from 1,3-Dithiole-2-thiones using a High-pressure Reaction

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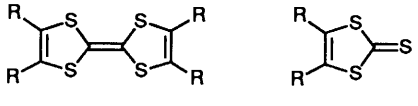
Tetrathiafulvalenes such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) having alkylthio substituents have been prepared in good yields by direct desulphurization of 1,3-dithiole-2-thiones with trimethyl phosphite under high pressure.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) **1a** is an important component of organic superconductors [1] and several methods of preparing it have been developed.[2] Although the simplest route for the synthesis is desulphurization of the readily available 1,3-dithiole-2-thione **2a** with trivalent phosphorus compounds, the reaction is smooth only under photochemical conditions.[3] Therefore, the thione **2a** is usually converted into the corresponding 1,3-dithiol-2-one by reaction with $Hg(OAc)_2$



1 **a**; R, R = SCH_2CH_2S **2**
b; R = SMe
c; R = $S(CH_2)_9Me$
d; R = H

followed by deoxygenation.[2,4] We have now examined desulphurization of the thiones **2a–d** under high pressure and found that the reaction to afford the TTF derivatives **1a–d** is accelerated by high pressure.

The thione **2a** and trimethyl phosphite failed to react at atmospheric pressure but when heated in toluene under high pressure gave BEDT-TTF in fairly high yield. The product was isolated pure by filtration or could be crystallized by addition of ethanol to the reaction mixture. The effects of pressure, temperature and reaction time were investigated in detail and the results are summarized in Table 1. A change in pressure from 400 to 800 MPa had no effect on the yield of BEDT-TTF whilst

Table 1 Desulphurization of the thiones **2** under various conditions[a]

Thione 2	Pressure (MPa)	Temp. (°C)	Time (h)	Product	Yield (%)
a	800	80	24	**a**	82
a	800	25	24	**a**	< 5
a	400	100	6	**a**	75
a	400	80	6	**a**	78
a	10^{-1}	80	24	**a**	0
b	800	80	6	**b**	48
b	400	80	6	**b**	50
c	500	80	24	**c**	54
c	400	80	6	**c**	60
d	800	80	6	**d**	14
d	400	80	6	**d**	30

[a] In the presence of 12 equiv. of $P(OMe)_3$ in toluene.

a period of 6 h at 80 °C was sufficient for the reaction to take place. Similarly (400 MPa at 80 °C for 6 h), the methylthio thione **2b** gave the corresponding TTF derivative **1b** in moderate yield. The TTF derivative **1c** with long alkyl chains, which is of interest as a one-component organic semiconductor,[5] was also obtained by direct desulphurization of the thione **2c**. The higher yield of **1a** compared with the yields of **1b** and **1c** may be due to the lower solubility of the former in solvents leading to easy crystallization. Use of triethyl phosphite rather than trimethyl phosphite as the desulphurization reagent had no significant effect on the yield of the TTF derivatives. Use of triphenylphosphine however gave an adduct of the latter instead of the desired TTF derivative.

Although attempted preparation of the parent TTF **1d** by desulphurization of the thione **2d** or deoxygenation of the corresponding ketone was reported to be unsuccessful,[6] the high-pressure reaction did give the compound (see Table 1), albeit in lower yield than the yields for other derivatives.[7] These results show that the high-pressure reaction is a simple and useful method for the preparation of TTF derivatives.

References

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6 TTF is usually synthesized by a coupling reaction of 1,3-dithiolium which is prepared from **2d** *via* several steps (F. Wudl, M. L. Kaplan, E. J. Hufnagel and E. W. Southwick, Jr., *J. Org. Chem.*, 1974, **39**, 3608.
7 The TTF produced was purified by column chromatography on silica gel.

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