Key Intermediates for the Synthesis of Organic Semiconductors: a Direct Dithiocarbamate Route to Unsubstituted 1,3-Dithiol-2-one Derivatives†

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Acid-catalyzed cyclization of formylmethyl piperidine-1-carbodithioate dimethyl or diethyl acetals (**2a,b**) at elevated temperatures is a key step in a convenient route to 1,3-dithiole-2-thione (**1b**) and 1,3-dithiole-2-selone (**1c**) *via* the unsaturated dithiolium salt (**4**); attempted cyclizations of (**2a**) and (**2b**) at lower temperatures led to alkoxy-substituted dithiolium salts (**3a**) and (**3b**).

Thio- and seleno-carbonyl derivatives of 1,3-dithiol-2-one (**1a**) are key intermediates in the synthesis of tetrathiafulvalene (TTF) and its analogues,[1–4] the reported preparations of which are often time-consuming and tedious.[5–14] A direct method for the preparation of these compounds *via* alkylation of dithiocarbamate salts with 2-halogenoacetaldehyde acetals followed by cyclization of the intermediate dithiourethane, which is widely used in the preparation of substituted dithiol-2-one derivatives,[1] is reported to be unsuccessful for the unsubstituted compounds.[7] Similar difficulties have also been noted in the attempted direct preparation of 1,3-diselenol-2-one

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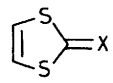
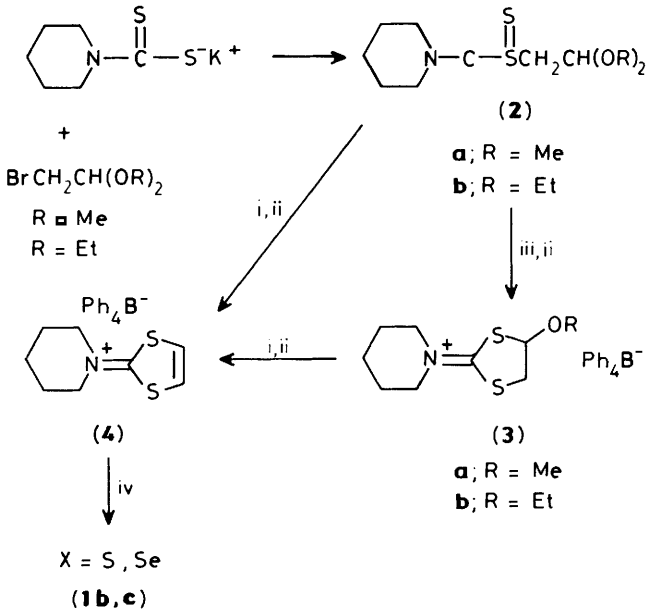


(1)

a; X = O
b; X = S
c; X = Se

derivatives.[15] We report that such an alkylation–cyclization route, in fact, provides a convenient route for the preparation of the unsubstituted dithiole-2-thione (**1b**) and -selone (**1c**).

Treatment of potassium piperidine-1-carbodithioate with a bromoacetaldehyde acetal in refluxing acetone affords in good yield formylmethylpiperidine-1-carbodithioate dimethyl or diethyl acetals (**2a**) and (**2b**) (Scheme). Both acetals cyclize in



Scheme. *Reagents and conditions:* i, H_2SO_4 at 55—60 °C; ii, $NaBPh_4$; iii, H_2SO_4 at 0 °C or CF_3CO_2H at reflux; iv, NaHX.

sulphuric acid at 55—60 °C to afford the desired iminium tetraphenylborates (**4**). However, if the acid-catalyzed cyclization step is attempted at lower temperatures, only intermediate alkoxy-substituted dithiolium salts (**3a**) and (**3b**) are obtained. These are converted into the unsaturated iminium derivative (**4**) upon acid treatment at elevated temperatures. Compound (**4**) can be readily converted into dithiol-2-one derivatives (**1b**) and (**1c**) by treatment with sodium hydrogen sulphide or sodium hydrogen selenide.

The conditions necessary for cyclization–elimination of the unsubstituted dithiourethanes (55—60 °C) are much more vigorous than those required for the reaction of the dialkyl-substituted derivatives which readily cyclize and eliminate at low temperatures (0—5 °C), presumably due to a decreased stabilization of the carbocationic character of the intermediate in the reaction of the unsubstituted compounds.[16] These more vigorous conditions for the elimination, in all likelihood, led to the failure of the alkylation–cyclization carbamate route to dithiole derivatives previously described.

Experimental

Compounds (**1b**) *and* (**1c**).—Carbon disulphide (7.2 ml, 0.12 mol) and benzene (25 ml) were added to a vigorously stirred mixture of piperidine (8.5 g, 0.10 mol), potassium hydroxide (6.7 g, 0.12 mol), and water (5 ml). The mixture was stirred for 4 h and then evaporated to dryness to afford yellow crystals. A solution of these in hot acetone was filtered and diluted with light petroleum to give the product. Recrystallization of this from chloroform and acetone–light petroleum afforded colourless crystals of the potassium dithiocarbamate (90%).

A vigorously stirred mixture of the potassium dithiocarbamate (8.0 g, 40.2 mmol) and bromoacetaldehyde diethyl acetal (7.9 g, 40.2 mmol) in acetone (200 ml) was heated to reflux overnight. After cooling to room temperature, the mixture was filtered and the filtrate concentrated under reduced pressure. The residue was dissolved in light petroleum (200 ml) and the solution filtered and evaporated to afford the diethyl acetal (**2b**) as a colourless solid. Recrystallization of this from absolute ethanol afforded (**2b**) (70%), m.p. 46.5—48 °C.* Analogously, the dimethyl acetal derivative (**2a**) was obtained (89%), m.p. 56—59 °C. Three recrystallizations from ethanol afforded an analytically pure sample of (**2a**) m.p. 58.5—60 °C.

The acetal (**2b**) (30 g) was added to concentrated sulphuric acid (150 ml)–ether (6 ml) at 0—5 °C, and the mixture heated overnight with stirring at 55—60 °C. It was then poured into water (390 ml), and sodium tetraphenylboron (37.2 g) in water (600 ml) was added and the mixture stirred for 1 h at room temperature. The resulting solid was filtered off and dried *in vacuo*. Recrystallization from acetonitrile afforded 2-piperidino-1,3-dithiolium tetraphenylboron (**4**) as colourless crystals, m.p. 206 °C (decomp.). Alternatively, the acetal (**2b**) (15 g) was heated overnight in trifluoroacetic acid (36 ml) to effect cyclization and afford the corresponding ethoxydithiolium species. This solution was added to concentrated sulphuric acid (75 ml) and the mixture stirred at 60 °C for 8 h; it was then cooled to 10 °C. Sodium tetraphenylboron (18.5 g) was added to the mixture and compound (**4**) filtered off and dried (43%).

If the reaction of the acetal (**2a**) or (**2b**) was terminated prior to the sulphuric acid treatment and sodium tetraphenylboron added, the alkoxy dithiolium salts (**3a**), m.p. 179—181 °C (decomp.) and (**3b**) m.p. 156.5—157.5 °C could be isolated in 30 and 63% yields respectively. Lower yields of (**3a**) and (**3b**) could be obtained by treatment of the acetals with sulphuric acid at 0—5 °C and analogous work-up.

Treatment of the tetraphenylboron salt (**4**) (7.6 g, 15.0 mmol) in DMF (46 ml)–acetic acid (23 ml) with sodium hydrogen sulphide hydrate (2.76 g, 30.1 mmol) and stirring overnight at 60 °C, followed by aqueous work-up and ether extraction afforded the crude 1,3-dithiole-2-thione (**1b**). Purification by flash chromatography (silica–dichloromethane) afforded the pure thione (**1b**) (54%), m.p. 49—50 °C (lit.,[13] 49.5 °C). Similarly, 1,3-dithiole-2-selone (**1c**) was obtained when the tetraphenylboron salt (**4**) (2.8 g) was added to a solution of sodium hydrogen selenide (5.7 mmol) in DMF (12 ml)–acetic acid (6 ml), and the mixture stirred for 2 days at room

* Spectra (**2a**): δ($CDCl_3$) 4.60 (t, 1 H), 4.51 (br s, 2 H), 3.96 (br s, 2 H), 3.62 (d, 2 H), 3.44 (s, 6 H), 1.71 (br s, 6 H); $\nu_{max.}$(KBr) 3 000—2 850, 1 470, 1 420, 1 230, 1 100, 1 050, 890, and 850 cm^{-1}. (**2b**): δ_H($CDCl_3$) 4.73 (t, 1 H), 4.32 (br s, 2 H), 3.98 (br s, 2 H), 3.84—3.64 (m, 4 H), 3.62 (d, 2 H), 1.73 (br s, 6 H), 1.24 (t, 6 H); $\nu_{max.}$(KBr) 2 935, 1 475, 1 425, 1 230, 1 110, and 970 cm^{-1}. (**3a**): δ[$(CD_3)_2SO$] 7.40—6.75 (complex, 20 H), 6.32—6.22 (m, 1 H), 4.36—4.10 (m, 2 H), 4.04—3.84 (m, 4 H), 3.44 (s, 3 H), 1.90—1.52 (m, 6 H); $\nu_{max.}$(KBr) 3 052, 2 949, 1 551, 1 442, 1 197, 1 075, 703, and 700 cm^{-1}. (**3b**): δ[$(CD_3)_2SO$] 7.3—6.7 (complex, 20 H), 6.30 (d, 1 H), 4.16 (m, 2 H), 3.84 (m, 4 H), 3.64 (m, 2 H), 1.74—1.52 (br m, 6 H), and 1.16 (t, 3 H); $\nu_{max.}$(KBr) 3 145, 1 571, 1 569, 1 076, 731 and 702 cm^{-1}. (**4**): δ[$(CD_3)_2SO$] 7.8—6.7 (complex, 22 H), 4.8—4.5 (m, 4 H), and 1.9—1.4 (m, 6 H); δ_C[$(CD_3)_2SO$] 187.9, 164.7, 162.7, 161.7, 135.5, 125.3, 125.25, 125.18, 125.13, 124.0, 121.4, 24.3, and 21.1; $\nu_{max.}$(KBr) 3 100—2 850, 1 570, 1 440, 1 350, 730, 700, and 600 cm^{-1}.

temperature. Aqueous work-up and ether extraction followed by flash chromatography (silica gel–dichloromethane) afforded pure selone (**1c**) (40%), m.p. 62 °C (lit.[13] 59—60 °C).

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