Synthesis of Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)

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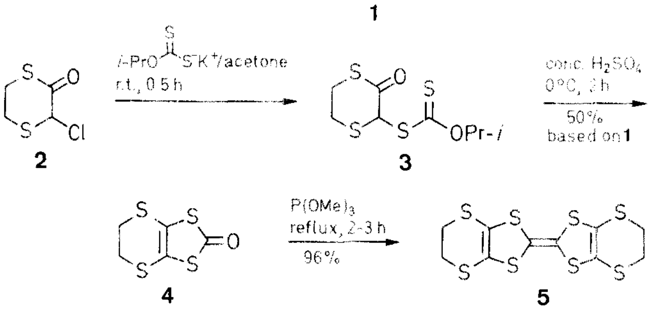
2-Oxo-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (**4**) was prepared in four steps from cheap starting materials in high overall yield. Coupling of **4** with trimethyl phosphite in toluene gave bis(ethylenedithio)tetrathiafulvalene (**5**; BEDT-TTF; 2,2′-bi-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiinylidene) in 96% yield.

BEDT-TTF (2,2′-bi-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiinylidene has been used extensively in the preparation of new superconducting molecular solids.[2-6] In our need for relatively large amounts of high purity BEDT-TTF we have developed a method to prepare BEDT-TTF, which avoids the troublesome and hazardous reduction of carbon disulfide with alkali metals[7] and the following time-consuming work-up.[8-11]

We here describe a synthesis of BEDT-TTF which offers the following advantages:

Cheap and readily available starting materials, good yields in all steps, large scale (15 grams or more) of BEDT-TTF, and relatively short reaction times for each step.



The synthesis is outlined in the scheme. A similar synthesis of BEDT-TTF homologues has been reported previously by Schumaker et al.[12] Compound **1** has been made earlier by Hiroi et al.[13] on a small scale. The α-halogenation of **1** is accomplished by *N*-chlorosuccinimide (NCS) in carbon tetrachloride.[14] Stirring a mixture of **2** and potassium *O*-(*i*-propyl) dithiocarbonate in dry acetone for 0.5 h at room temperature gives **3**. Cyclization of **3** in concentrated sulfuric acid gives **4** in 50% yield based on **1**.

2-Oxo-1,4-dithiane (1):
To a mechanically stirred solution of 1,2-ethanedithiol (51 mL, 0.6 mol) and NEt$_3$ (168 mL, 1.2 mol) in dry CH$_2$Cl$_2$ (600 mL) is added dropwise and with ice cooling chloroacetyl chloride (48 mL, 0.6 mol) in dry CH$_2$Cl$_2$ (300 mL). After the addition (1 h) the solution is stirred for 2 h at room temperature. The precipitate is filtered off and washed with CH$_2$Cl$_2$ (2 × 75 mL). The combined organic phases are washed with H$_2$O (3 × 75 mL) and dried (MgSO$_4$). The solvent is evaporated, and the crude product is distilled *in vacuo*, bp 92–93 °C/0.7 Torr (Lit.[13] bp 105 °C/3 Torr). Yield: 48 g (60%).

^{1}H-NMR (CDCl$_3$/TMS): δ = 3.2 (m).

^{13}C-NMR (CDCl$_3$/TMS): δ = 25.82 (s, CH$_2$); 31.02 (s, CH$_2$); 35.25 (s, CH$_2$); 197.11 (s, C=O).

3-Chloro-2-oxo-1,4-dithiane (2):
A stirred solution of **1** (4.0 g, 0.03 mol) and NCS (4.0 g, 0.03 mol) in dry CCl$_4$ (100 mL) is heated to reflux for 10–15 min. After cooling to 0 °C and filtration the solvent is removed at reduced pressure, and the product is obtained in quantitative yield as a slightly yellow oil. **2** is used in the following step without further purification.

^{1}H-NMR (CDCl$_3$/TMS): δ = 3.2 (m, 4H, CH$_2$); 5.37 (s, 1H, CH).

^{13}C-NMR (CDCl$_3$/TMS): δ = 24.52 (s, CH$_2$); 30.18 (s, CH$_2$); 61.91 (s, CH); 188.27 (s, C=O).

2-Oxo-3-(*i*-propoxythiocarbonylthio)-1,4-dithiane (3):
Compound **2** (5.1 g, 0.03 mol) is stirred with potassium *O*-(*i*-propyl) dithiocarbonate (5.2 g, 0.03 mol) in dry acetone (200 mL) at room temperature for 0.5 h. The precipitate is filtered off, and the solvent is removed at reduced pressure. Compound **3** is obtained in quantitative yield as a bright red oil and used in the following step without further purification.

^{1}H-NMR (CDCl$_3$/TMS): δ = 1.40 (d, 6H, CH$_3$); 3.41 (m, 4H, CH$_2$); 5.62 (s, 1H, CH); 5.70 (sept, 1H, CH).

^{13}C-NMR (CDCl$_3$/TMS): δ = 21.00 (s, CH$_3$); 27.70 (s, CH$_2$); 31.74 (s, CH$_2$); 54.17 (s, CH); 79.53 (s, CH); 191.58 (s, CO); 207.71 (s, CS).

2-Oxo-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (4):
Compound **3** (8.1 g, 0.03 mol) is added in small portions to conc. H$_2$SO$_4$ (300 mL) at 0 °C. After 2 h the mixture is poured on ice (1 L) and extracted with toluene (3 × 200 mL). The combined organic phases are washed with H$_2$O (4 × 75 mL), dried (MgSO$_4$), and the solvent is evaporated. Recrystallization from toluene gives **4** as white crystals; yield: 3.2 g (50% based on **1**; mp 126–127 °C (Lit.[8] mp 127–128 °C.

2,2′-Bi-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiinylidene (5; BEDT-TTF):
Compound **4** (4.18 g, 0.02 mol) is heated to reflux in P(OMe)$_3$ (60 mL). The solution is refluxed for 2–3 h, during which bright orange-red crystals precipitated. The mixture is cooled to room temperature, filtered, washed with CH$_3$OH (50 mL) and Et$_2$O (50 mL), and dried (vacuum) to provide 3.7 g (96%) of BEDT-TTF. Recrystallization from PhCl afforded **4** as bright red needles; mp 245–247 °C (dec) (Lit.[8] mp 246–248 °C (dec).

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