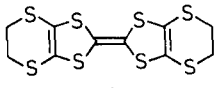
Generation and Trapping of Phosphorus Stabilized 4,5-Ethylenedithio-1,3-dithiol-2-ide Carbanions: Synthesis of Ethylenedithio-1,3-dithiafulvalenes

Adrian J. Moore, Martin R. Bryce*
Department of Chemistry, University of Durham, Durham, DH1 3LE, England

2-Dimethoxyphosphoryl-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]-2-dithiin **(8)** and 2-triphenylphosphonio-5,6-dihydro-1,3-dithiolo-[4,5-*b*][1,4]dithiin tetrafluoroborate **(9)** have been obtained in four steps from 4,5-ethylenedithio-1,3-dithiole-2-thione **(4)** (ca. 75% overall yield). Deprotonation of **(8)** and **(9)** yields the corresponding carbanion **(10)** and ylide **(11)** which have been trapped in good yield with glyoxal, cyclopentanone and anthraquinone to afford ethylenedithio-1,3-dithiafulvalenes.

The synthesis of derivatives and analogues of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) **(1)** is of considerable current interest.[1-5] Many of these molecules are readily oxidised to stable radical cations which are components of conducting and superconducting salts.[6,7]

Phosphoranes and phosphonate esters of benzo-1,3-dithiole,[8-11] 1,3-dithiole,[12-14], 1,3-selenathiole[14] and 1,3-diselenole,[15] i.e. molecules of general formulae **2** and **3**, are known to be valuable synthetic intermediates. These highly reactive systems, which are formally hetero-antiaromatic, 8π, anions, react readily with carbonyl compounds to yield dithiafulvenes.[16] They have also been used in the synthesis of unsymmetrical tetrathiafulvalenes.[9,13,14] We now report analogous methodology for the efficient preparation of ethylenedithio-1,3-dithiafulvenes: the key step is the generation and trapping of the hitherto unknown 2-(dimethoxyphosphoryl)-1,3-dithiol-2-ide carbanion **10** and phosphorane **11**. The conversion of thione **4** into cation **7** has been reported previously, but synthetic details were not given.[17] This sequence is based on a route to the 1,3-dithiolium cation initially developed by Wudl and co-workers.[18]



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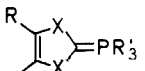
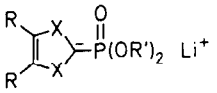


2

R = H, alkyl, ester
R' = alkyl, phenyl
X = S or Se

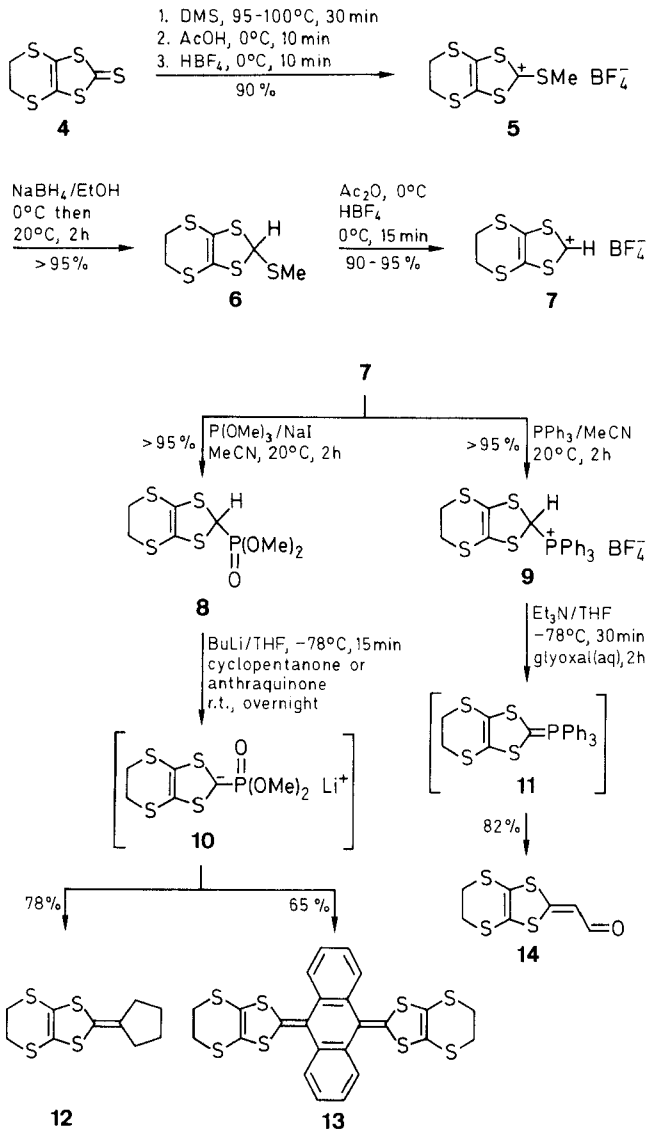


3

R = H, alkyl
R' = alkyl
X = S or Se

Thione **4**[4,5] was methylated using dimethyl sulphate to yield cation **5** which was isolated and purified as its crystalline tetrafluoroborate salt. Cation **5** was reduced by sodium borohydride to yield compound **6** which was isolated as an oil that could be purified by column chromatography. However, compound **6** was almost analytically pure in the crude state, so purification was not usually performed at this stage. Conversion of compound **6** into cation **7** occurred readily upon treatment with acetic anhydride followed by addition of tetrafluoroboric acid. Recrystallization afforded cation salt **7** as a white solid. The yield of purified product from each of the three steps described above was in excess of 90%. Cation **7** yielded phsophonate ester **8** (> 95% yield) on treatment with trimethyl phosphite in the presence of sodium iodide; the corresponding phosphonium salt **9** was obtained from cation **7** and triphenylphosphine (> 95% yield). Compound **9** is shelf-stable at room temperature, whereas compound **8** darkens slowly on exposure to air or daylight.

The generation of carbanion **10** and ylide **11** from reagents **8** and **9**, respectively, proceeded smoothly under basic conditions. Aqueous glyoxal underwent a Wittig reaction with intermediate **11** (generated using triethyl-



amine as base at room temperature) to yield aldehyde **14** (82% yield) which is a potential precursor to vinylogous BEDT-TTF systems.[10,19] Intermediates **10** and **11** were both trapped with cyclopentanone to yield ethylenedithio-1,3-dithiafulvalene derivative **12**; when butyllithium was used as base, at −78 °C the yield of product **12** was higher from phosphonate ester **8** (78%) than from phosphonium salt **9** (62%). Akiba and co-workers have reported similar increased reactivity of phosphonate ester anions of 1,3-dithiole systems **3** over their phosphonate analogues **2**.[16] When triethylamine was used as base at room temperature for the generation of ylide **11**, the trapping reaction was far less efficient; product **12** formed in only 25% yield. Reaction of anion **10** with anthraquinone yielded compound **13** (65% yield) which is the first *p*-quinodimethane analogue of BEDT-TTF **1** to be reported.

Cyclic voltammetry of electron donor molecule **13** shows a single, two-electron, quasi-reversible oxidation to the dication at $E_{ox} = +0.48$ V. This oxidation potential is lower than the first oxidation potential of BEDT-TTF (**1**) ($E_1^{\frac{1}{2}} = +0.58$ V, $E_2^{\frac{1}{2}} = +0.99$ V, measured under identical conditions) indicating that the extended system **13** is the better donor. The reductive peak for compound **13**, i.e. donor^{2+} → donor^0, is observed at $E_{red} = +0.35$ V which is a markedly higher potential than that found for other extended anthracenediylidene derivatives, e.g. 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene.[11,14] This is consistent with the known destabilising effect of an ethylenedithio substituent fused to a 1,3-dithiolium cation.[20]

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 577 and 547 spectrophotometers; ultra-violet spectra were recorded on a Kontron Uvikon 930 instrument. ^{1}H-NMR spectra were recorded on a Bruker AC 250 instrument, operating at 250.134 MHz; chemical shifts, given in ppm, are relative to TMS as internal standard. Mass spectra were obtained on a VG 7070E instrument, operating at 70 eV, with ionisation modes as indicated. All solvents were distilled prior to use in chromatography. Solvents were dried from the following agents under a nitrogen atmosphere: THF (sodium metal then $LiAlH_4$); acetonitrile (CaH_2). Cyclic voltammetry experiments were performed in a one-compartment cell with platinum working and counter electrodes and a silver/silver chloride reference electrode. Measurements were made with a BAS 100 electrochemical analyser and were iR compensated. The cell contained a solution of donor (ca. 1×10^{-5} M) with oven-dried (120 °C) tetrabutylammonium perchlorate (TBAP) (0.01 M) as supporting electrolyte in dry MeCN (ca. 10 mL); all solutions were purged with argon and retained under the inert atmosphere while the CV data were recorded.

2-Methylthio-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ium Tetrafluoroborate (5):

A stirred suspension of compound **4**[4] (1.10 g, 4.9 mmol) in dimethyl sulphate (5 mL) is heated at 95–100 °C for 30 min or until dissolution is complete. The mixture is cooled to 0 °C and AcOH (glacial, 1 mL) is added. After stirring for a further 10 min, diethyl ether–tetrafluoroboric acid (0.80 g, 4.9 mmol) is added and stirring continued for 10 min. Et_2O (75 mL) is added, precipitating an orange solid which is collected by filtration and washed thoroughly with Et_2O (5 × 30 mL). Recrystallization from MeOH affords salt **5** as an orange solid; yield: 1.47 g (92%); mp 124–126 °C (dec).

$C_6H_7BF_4S_5$	calc.	C 22.08	H 2.16	S 49.14
(326.2)	found	21.75	2.03	49.47

^{1}H-NMR (DMSO-d_6/TMS): $\delta = 3.24$ (s, 3H, SCH_3), 3.66 (s, 4H, SCH_2).

2-Methylthio-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (6):

Finely-ground $NaBH_4$ (0.17 g, 4.5 mmol) is added portionwise over 30 min to a stirred suspension of salt **5** (1.45, 4.44 mmol) in dry EtOH (30 mL) at 0 °C under nitrogen. The mixture is stirred for a further 2 h at 20 °C; the solvent is evaporated, water (30 mL) added and the residue extracted with CH_2Cl_2 (3 × 30 mL). The organic layer is dried ($MgSO_4$) and concentrated *in vacuo* to afford the crude product **6** as a red oil of sufficient purity for further reaction; yield: 1.00 g (95%). Purification of compound **6** is achieved by chromatography on a silica gel column (10 cm × 2 cm, 70–230 mesh) eluting with cyclohexane/CH_2Cl_2 (1:1 v/v).

$C_6H_8S_5$	calc.	C 29.97	H 3.35	S 66.68
(240.4)	found	29.75	3.29	66.96

MS (EI): $m/z = 240$ (M^+).

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 2.18$ (s, 3H, CH_3), 3.12–3.36 (AA'BB', 4H, SCH_2), 5.84 (s, 1H, CH).

5,6-Dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ium Tetrafluoroborate (7):

Diethyl ether–tetrafluoroboric acid (0.72 g, 4.5 mmol) is added dropwise over 10 min to a stirred solution of compound **6** (1.00 g, 4.1 mmol) in Ac_2O (10 mL) at 0 °C under nitrogen. After stirring for a further 15 min, dry Et_2O (100 mL) is added and stirring continued for 30 min. The solid is collected by filtration and washed thoroughly with Et_2O (3 × 40 mL). Recrystallisation from

EtOH affords salt **7** as a white solid; yield: 1.03 g (90%); mp ca. 110°C (dec).

$C_5H_5BF_4S_4$ (280.2) calc. C 21.43 H 1.80 S 45.78
found 20.09 1.63 45.27

^{1}H-NMR (DMSO-d_6/TMS): δ = 3.53 (s, 4H, SCH_2), 6.73 (s, 1H, CH).

2-Dimethoxyphosphoryl-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (8):
Trimethyl phosphite (0.42 mL, 3.60 mmol) and NaI (0.54 g, 3.60 mmol) are added successively to a stirred solution of salt **7** (1.00 g, 3.57 mmol) in dry MeCN (50 mL) at 20°C under nitrogen. The mixture is stirred for a further 2 h at 20°C; the solvent is evaporated, water (25 mL) added and the residue extracted with CH_2Cl_2 (3 × 25 mL). The organic layer is dried ($MgSO_4$) and evaporated *in vacuo* to afford an off-white solid. Recrystallisation from EtOH/cyclohexane affords compound **8** as a white solid; yield: 0.92 g (95%); mp 102–103°C.

$C_7H_{11}O_3PS_4$ (302.4) calc. C 27.80 H 3.67 S 42.41
found 27.92 3.61 42.17

MS (EI): m/z = 302 (M^+).

IR (KBr): ν = 1040 (vbr, P–O–C), 1235 cm^{-1} (vbr, P=O).

^{1}H-NMR ($CDCl_3$/TMS): δ = 3.18–3.39 (AA'BB', 4H, SCH_2), 3.93 (d, 10.4 Hz, CH, OCH_3, 4.83 (d, 1H, J = 6.8 Hz, CH).

2-Triphenylphosphonio-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin Tetrafluoroborate (9):
Triphenylphosphine (0.94 g, 3.57 mmol) is added to a stirred solution of salt **7** (1.00 g, 3.57 mmol) in dry MeCN (30 mL) at 20°C under nitrogen. Stirring is continued for 2 h, the solvent is then evaporated *in vacuo* and the residue washed thoroughly with Et_2O (5 × 50 mL). Recrystallisation from EtOH/cyclohexane affords salt **9** as a white solid; yield: 1.72 g (89%); mp 183–185°C.

$C_{23}H_{20}BF_4PS_4$ (542.4) calc. C 50.92 H 3.72 S 23.65
found 51.07 3.58 23.97

^{1}H-NMR (DMSO-d_6/TMS): δ = 2.85–3.10 (AA'BB',4H, SCH_2), 7.90 (m, 6H_{arom}), 8.02 (m, 9H_{arom}), 8.26 (s, 1H, CH).

2-Cyclopentylidene-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (12):
BuLi (1.6 M, 0.62 mL, 1.0 mmol) is added to a stirred solution of compound **8** (250 mg, 0.92 mmol) in dry THF (40 mL) at –78°C under nitrogen. After 15 min, cyclopentanone (0.08 mL, 0.92 mmol) is added and the mixture allowed to warm to 20°C overnight. The solvent is evaporated *in vacuo*, water (30 mL) added and the residue extracted with CH_2Cl_2 (3 × 25 mL). The organic layer is dried ($MgSO_4$) and evaporated *in vacuo*. Chromatography of the residue on silica gel (10 cm × 2 cm, 70–230 mesh) eluting with CH_2Cl/cyclohexane (1:1 v/v) affords compound **12** as a yellow solid; yield: 187 mg (78%); mp 130–131°C.

$C_{10}H_{12}S_4$ (260.4) calc. C 46.11 H 4.65 S 49.24
found 46.32 4.49 49.15

MS (EI): m/z = 260 (M^+).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.72 (m, 4H, CH_2), 2.08 (m, 4H, CH_2), 3.29 (s, 4H, SCH_2)

9,10-Bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-9,10-dihydroanthracene (13):
BuLi (1.6 M, 0.62 mL, 1.0 mmol) is added to a stirred solution of compound **8** (250 mg, 0.92 mmol) in dry THF (40 mL) at –78°C under nitrogen. After 15 min, a suspension of anthraquinone (95 mg, 0.46 mmol) in dry THF (5 mL) is added and the mixture allowed to warm to 20°C overnight. Work up as for compound **12** affords compound **13** as a yellow-orange solid; yield: 168 mg (65%); mp 196–197°C.

$C_{24}H_{16}S_8$ (560.9) calc. C 51.39 H 2.88 S 45.73
found 51.51 2.66 45.76

MS (EI): m/z = 560 (M^+).

UV (MeCN): λ = 238, 269, 440 nm.

^{1}H-NMR ($CDCl_3$/TMS): δ = 3.28 (s, 8H, SCH_2), 7.31 and 7.50 (AA'XX', each 4H_{arom}).

2-Formylmethylene-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (14):
Dry triethylamine (0.38 mL, 2.75 mmol) is added to a stirred suspension of salt **9** (1.50 g, 2.75 mmol) in dry THF (40 mL) at 20°C under nitrogen. After 30 min, glyoxal (40 wt.% in water, 0.80 g, 5.5 mmol) is added and stirring continued for 2 h. The solvent is evaporated *in vacuo* and the residue chromatographed on a silica gel column (15 cm × 3 cm, 70–230 mesh) eluting with CH_2Cl_2/cyclohexane (2:1 v/v) to afford compound **14** as a yellow-orange solid; yield: 0.53 g (82%); mp 125–126°C.

$C_7H_6OS_4$ (234.4) calc. C 35.87 H 2.58 S 54.72
found 35.56 2.81 54.48

MS (EI): m/z = 234 (M^+).

IR (KBr): ν = 1605 (C=C), 1620 cm^{-1} (C=C–CHO).

^{1}H-NMR ($CDCl_3$/TMS): δ = 3.33 (s, 4H, SCH_2), 6.62 (d, 2.6 Hz, 1H, CH), 9.38 (d, 1H, J = 2.6 Hz, CHO).

Addendum. Since submission of this manuscript we have learned that **14** has been prepared by two other groups using similar methodology.[21]

We thank SERC for financial support for this work.

Received: 17 August 1990

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