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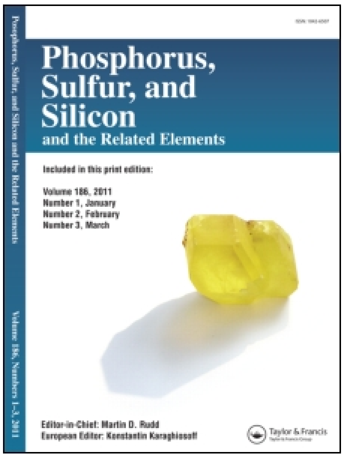

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REACTION OF 1,2-DITHIOLANE WITH α-LITHIATED THIOPHENES: SELECTIVE SYNTHESES OF MONO-*S*-THIENYL-1,3-PROPANEDITHIOLS

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REACTION OF 1,2-DITHIOLANE WITH α-LITHIATED THIOPHENES: SELECTIVE SYNTHESES OF MONO-*S*-THIENYL-1,3-PROPANEDITHIOLS

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Lithiated thiophenes **3** cleaved S—S bond of 4,4-disubstituted 1,2-dithiolane **1** and naphthalene-1,8-disulfide **5** to give the ring opened products **2** and **6**, respectively, in excellent yields.

Key words: Cyclic disulfides; 4,4-disubstituted 1,2-dithiolane; nucleophilic S—S bond cleavage; lithiated thiophenes; mono-S-thienyl-1,3-propanedithiols; S3 ligands for transition metals.

INTRODUCTION

The nucleophilic bond cleavage of 1,2-dithiolanes **1** and naphtho[1,8-*c*,*d*]-1,2-dithiole **5** resulted in a quantitative ring-opening.[1] The products were the 1,3-propanedithiol derivatives, one SH group of which was selectively functionalized by the nucleophiles employed. One of the most important applications of these reactions would be the synthesis of asymmetric sulfur containing ligands for transition metals.[2] Unexpected results were also reported.[3]

Thiophenes **4** are known to be readily lithiated with butyllithium to give α-lithiothiophenes **3**.[4] They reacted with 1,2-dithiolanes **1** and naphthalene-1,8-disulfide **5** in a straight forward manner to give excellent yields of thiophene containing ligands **2** and **6**.

RESULTS AND DISCUSSION

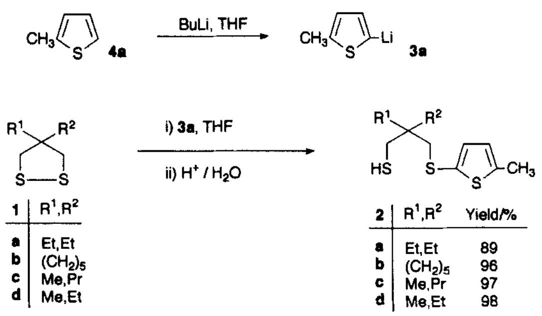
Methylthiophene **4a** was lithiated in THF with BuLi at room temperature for 30 min (see Scheme 1). A slight excess of thiophene was used to assure complete consumption of BuLi which may otherwise react with 1,2-dithiolane to give undesired products. Then, 1,2-dithiolane **1** was added to the THF solution of 5-methyl-2-thienyllithium **3a** at room temperature and reacted for 30 min. After the usual workup, the product was separated by simple Kugelrohr distillation under reduced pressure. The results are summarized in Scheme 1. The products **2a–d** were those simply ring-opened by the α-carbanion **3a** of 2-methylthiophene **4a**. The structure of **2a** was confirmed by the following evidence: the parent peak (260) in MS spectra and relative intensity of the signals in the ^{1}H and ^{13}C NMR spectra showed the product **2a** contains dithiolanyl and thienyl moieties in 1:1 ratio. The characteristic triplet at 1.118 ppm coupled with a doublet at 2.538 ppm in its ^{1}H NMR spectra indicated the presence of —CH_2SH group, accompanied by a singlet at 2.874 ppm showing the presence of CH_2SAr. The 5-methyl-2-thienyl structure is consistent with the signals in ^{1}H NMR involving long range coupling (1 Hz) between 5-CH_3 and 4-H protons. The structures of **2b–d** were confirmed similarly.

The exclusive formation of **2** was confirmed by glc analyses showing the absence of non-thienylated 1,3-propanedithiols and bis-thienylated 1,3-propanedithiols in the reaction mixture. Products with high purity (>97%) were readily obtained in high yields (>89%) by simple isolation method in this synthetic reaction.

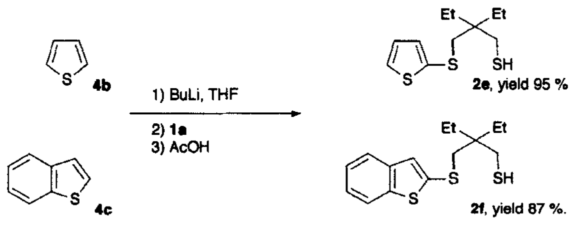
Non-substituted thiophene **4b** also gave the corresponding product **2e** in excellent yield (Scheme 2). The molar ratio of the reactants used, i.e.,

$$[\text{thiophene } \mathbf{4}]_0 > [\text{BuLi}]_0 > [\text{1,2-dithiolane } \mathbf{1}]_0 \quad (\text{or } [\mathbf{3}]_0 > [\mathbf{1}]_0)$$

was frequently employed to obtain the simple products in the case of **4a** and **4b**.



Scheme 1



Scheme 2

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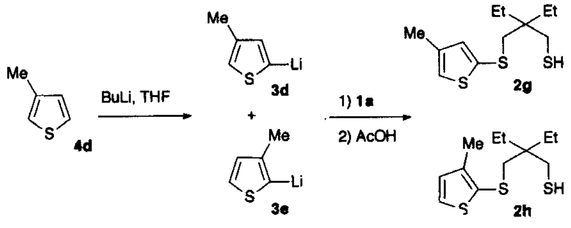
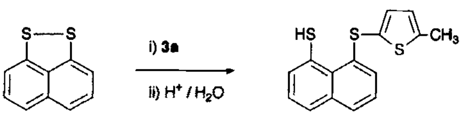


Mixture (**2g**:**2h** = 77:23), yield 96 %.

Scheme 3



5

6, yield 99 %.

Scheme 4

In the case of benzo[b]thiophene **4c**, the excess lithium reagent, 2-lithiobenzothiophene **3c**, further reacted with the ring-opened product (lithium salt of **2f**) giving a rather complicated mixture. Therefore, the molar ratio

$$[\mathbf{4c}]_0 > [\mathrm{BuLi}]_0 = [\mathbf{1a}]_0 \quad (\text{or } [\mathbf{3c}]_0 = [\mathbf{1a}]_0)$$

was essential to obtain the pure product **2f**.

In the case of 3-methylthiophene **4d** (Scheme 3), two isomeric lithium reagents **3d** and **3e** were generated to give the corresponding products **2g** and **2h** in a ratio of 77:23 as analyzed by glc using a 25 m capillary column.

Reaction of naphthalene-1,8-disulfide **5** with **3a** gave the expected product **6** in excellent yield (Scheme 4). Kugelrohr distillation of the products (ot 156–25°C/0.7 mmHg) resulted in a decrease in the yield (68%) and purity of the product (as judged by ^{1}H NMR) due to thermal decomposition.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-90 instrument operating at 90 and 22.5 MHz, respectively. DEPT methods using 90 and 135 degree pulses were employed to determine the number of proton(s) attached to the carbon. MS spectra were taken at 70 eV on a JEOL AX500 equipment. IR spectra were obtained by using a JASCO FT/IR-7000 spectrometer on KBr pellets of liquid samples.

All the dithiolanes **1a–d** were prepared from the corresponding 1,3-propanediols according to the reported method,[5] and distilled by Kugelrohr just before use. Naphthalene-1,8-disulfide **5** was prepared from diaminonaphthalene as previously reported.[6]

Reaction of **1a** *with 5-Methyl-2-Thienyllithium* **3a**. 2-Methylthiophene **4a** (225 mg, 2.30 mmol) and n-BuLi (2.0 mmol in hexane) were mixed in THF (5 ml) at room temperature for 30 min under argon. **1a** (171.6 mg, 1.06 mmol) was added to the solution and the mixture was stirred at room temperature for 30 min. The mixture was acidified with acetic acid (2 ml), diluted with water (15 ml), and extracted with dichloromethane (5 ml). The organic layer was concentrated under reduced pressure and distilled by Kugelrohr. **2a**. Yield 244 mg (89%). purity 97% by glc. ot. 115–135°C/0.7 mmHg. Found: C, 55.81; H, 7.78%; N, 0.12%. Calcd for $C_{12}H_{20}S_3$: C, 55.33; H, 7.74%. IR (KBr) ν 2968 (s), 2926 (m), 2880 (m), 2574 (vw, S—H), 1452 (m), and 797 cm^{-1} (m). ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.768 (6H, t, J = 7.4 Hz, 2CH$_3$), 1.118 (1H, t, J = 8.8 Hz, SH), 1.396 (4H, q, J = 7.4 Hz, 2CH$_2$), 2.424 (3H, d, J = 1.0 Hz, CH$_3$), 2.538 (2H, d, J = 9.0 Hz, $C\underline{H}_2SH$), 2.874 (2H, s, SCH$_2$), 6.572 (1H, dq, J = 3.5, 1.0

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Hz), and 6.906 ppm (1H, d, *J* = 3.5 Hz). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 7.56 ($2CH_3$), 15.62 (CH_3), 26.24 ($2CH_2$), 30.36 (CH_2SH), 41.02 (C), 45.94 (CH_2S), 125.40 (CH), 132.80 (C), 133.62 (CH), and 143.70 ppm (C). MS m/z (%) 260 (55, M), 143 (9, $Me(C_4H_2S)SCH_2^+$), 130 (100, $ME(C_4H_2S)SH$), 129 (32, $Me(C_4H_2S)S^+$), 97 (23, $MeC_4H_2S^+$), 85 (15).

2b–d were synthesized similarly and identified as follows: **2b.** yield 276 mg (from 183 mg **1b**) 96%. yellow oil, ot. 124–162°C/0.4 mmHg. Purity 99.6% (glc). Found: C, 57.52; H, 7.44%. Calcd for $C_{13}H_{20}S_3$: C, 57.30; H, 7.40%. IR (KBr) ν 2626 (s), 2856 (s), 2570 (w, SH), 1454 (s), 1294 (m), 1261 (m), 1214 (m), 1162 (m), 1065 (m), 797 (s), and 503 cm^{-1} (m). ^1H NMR ($CDCl_3$) δ 1.132 (1H, t, *J* = 9.0 Hz, SH), 1.420 (10H, broad s, $5CH_2$), 2.428 (3H, d, *J* = 1.0 Hz, CH_3), 2.656 (2H, d, *J* = 9.0 Hz, $C\underline{H}_2SH$), 2.996 (2H, s, SCH_2), 6.578 (1H, dq, *J* = 3.5 and 1.0 Hz), and 6.912 ppm (1H, d, *J* = 3.5 Hz). ^{13}C NMR ($CDCl_3$) δ 15.64 (CH_3), 21.52 ($2CH_2$), 25.98 (CH_2), 30.36 (CH_2), 34.06 ($2CH_2$), 38.18 (C), 47.22 (CH_2), 125.60 (CH), 133.00 (C), 133.62 (CH), and 143.72 ppm (C). MS m/z (%) 272 (32, M), 143 (16, $CH_2S(C_4H_2S)Me$), 142 (18), 130 (100), 129 (38, $S(C_4H_2S)Me$), 109 (48), 97 (30, $Me(C_4H_2S)$), 95 (30), 94 (16), 85 (24), 81 (44), 79 (18), 68 (18), 67 (88).

2c. yield 242 mg (from 155 mg **1c**) 97%. yellow oil, ot. 121–138°C/0.6 mmHg. Purity 99.8% (glc). Found: C, 55.46; H, 7.70%. Calcd for $C_{12}H_{20}S_3$: C, 55.33; H, 7.74%. IR (KBr) ν 2962 (s), 2930 (s), 2872 (s), 2572 (w, SH), 1444 (s), 1377 (m), 1214 (m), 1162 (m), 1065 (m), 953 (m), 797 (s), 501 cm^{-1} (m). ^1H NMR ($CDCl_3$) δ 0.982 (3H, s, Me), 1.162 (1H, t, *J* = 9.0 Hz, SH), 0.78–1.34 (7H, m, Pr), 2.428 (3H, d, *J* = 1.0 Hz, CH_3), 2.560 (2H, d, *J* = 8.5 Hz, $C\underline{H}_2SH$), 2.906 (2H s, SCH_2), 6.578 (1H, dq, *J* = 3.5 and 1.0 Hz), and 6.910 ppm (1H, d, *J* = 3.5 Hz). ^{13}C NMR ($CDCl_3$) δ 14.70 (CH_3), 15.62 (CH_3), 16.90 (CH_2), 23.16 (CH_3), 33.66 (CH_2), 38.72 (C), 40.28 (CH_2), 48.82 (CH_2), 125.58 (CH), 133.00 (C), 133.52 (CH), and 143.70 ppm (C). MS m/z (%) 260 (32, M), 143 (10, $CH_2S(C_4H_2S)Me$), 132 (10), 131 (16, M-$S(C_4H_2S)Me$), 130 (100), 129 (38, $S(C_4H_2S)Me$), 99 (10), 98 (10), 97 (38, $Me(C_4H_2S)$), 85 (24), 82 (10), 69 (18), 61 (10).

2d. yield 245 mg (from 151 mg **1d**) 98%. ot. 90–142°C/0.5 mmHg. Purity 99.5% (glc). Found: C, 53.85; H, 7.38%. Calcd for $C_{11}H_{18}S_3$: C, 53.61; H, 7.36%. IR (KBr) ν 2966 (s), 2922 (s), 2880 (s), 2570 (w, SH), 1460 (s), 1444 (s), 1379 (m), 1214 (m), 1162 (m), 1065 (m), 1004 (m), 953 (m), 797 (s), and 501 cm^{-1} (m). ^1H NMR ($CDCl_3$) δ 0.812 (3H, t, *J* = 7.5 Hz), 0.968 (3H, s, Me), 1.158 (1H, t, *J* = 9.0 Hz, SH), 1.430 (2H, q, *J* = 7.5 Hz), 2.424 (3H, d, *J* = 1.0 Hz, CH_3), 2.554 (2H, d, *J* = 9.0 Hz, $C\underline{H}_2SH$), 2.898 (2H, s, SCH_2), 6.576 (1H, dq, *J* = 3.5 and 1.0 Hz), and 6.906 ppm (1H, d, *J* = 3.5 Hz). ^{13}C NMR ($CDCl_3$) δ 8.02 (CH_3), 15.64 (CH_3), 22.62 (CH_3), 30.20 (CH_2), 33.20 (CH_2), 38.72 (C), 48.46 (CH_2), 125.58 (CH), 132.96 (C), 133.54 (CH), and 143.70 ppm (C). MS m/z (%) 246 (35, M), 143 (10, $CH_2S(C_4H_2S)Me$), 131 (12), 130 (100), 129 (44, $S(C_4H_2S)Me$), 117 (10, M-$S(C_4H_2S)Me$), 99 (12), 98 (14), 97 (30, $Me(C_4H_2S)$), 85 (28), 83 (32), 70 (20), 69 (18), 68 (12), 61 (16).

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Reaction of 4,4-Diethyl-1,2-dithiolane **1a** *with 2-Thienyllithium* **3b**. A hexane solution of n-BuLi (1.60 mmol) was added to a THF solution (5 ml) of freshly distilled thiophene (184 mg, 2.20 mmol) with stirring under argon at −78°C. After being stirred for 5 min at −78°C, the mixture was stirred at room temperature for 30 min. 4,4-Diethyl-1,2-dithiolane (216 mg, 1.33 mmol) was added to the mixture by means of a gas-tight syringe and stirred at room temperature for 30 min. The mixture was acidified with acetic acid (2 ml), diluted with water (10 ml), and extracted with dichloromethane (5 ml). The organic layer was concentrated and distilled by Kugelrohr to give **2e**. Yield 310 mg (95%), purity 99% by glc. ot. 160–190/20 mmHg. Found: C, 53.67; H, 7.33%. Calcd for $C_{11}H_{18}S_3$: C, 53.61; H, 7.36%. IR (KBr) ν 2968 (s), 2928 (m), 2880 (m), 2568 (vw, S—H), 1454 (m), 1218 (m), 847 (m), and 700 cm^{-1} (m). ^1H NMR ($CDCl_3$) δ 0.764 (6H, t, *J* = 7.4 Hz, $CH_2C\underline{H}_3$), 1.110 (1H, t, *J* = 8.8 Hz, SH), 1.394 (4H, q, *J* = 7.4 Hz, $CH_3C\underline{H}_2$), 2.540 (2H, d, *J* = 8.6 Hz, $HSC\underline{H}_2$), 2.920 (2H, s, SCH_2), 6.918 (1H, dd, *J* = 3.6, 5.2 Hz, H-4), 7.100 (1H, dd, *J* = 1.4, 3.6 Hz, H-3), and 7.278 ppm (1H, dd, *J* = 1.4, 5.2 Hz, H-5). ^{13}C NMR ($CDCl_3$) δ 7.54 ($2CH_3$), 26.24 ($2CH_2$), 30.34 (CH_2), 41.06 (C), 45.76 (CH_2), 127.42 (CH), 128.76 (CH), 132.92 (CH), and 135.98 ppm (C). MS m/z (%) 246 (94, M), 131 (52, M-SC_4H_3S), 130 (26), 129 (29, M-$CH_2SC_4H_3S$), 116 (100), 115 (43), 97 (84), 83 (45), 75 (37), 71 (73), 69 (34), 61 (27).

Reaction of **1a** *with Lithiated 3-Methyl-Thiophene* **4d**: 3-Methylthiophene **4d** (242.5 mg, 2.5 mmol) was lithiated with BuLi (2.0 mmol) in THF (5 ml) at room temp for 30 min under argon. **1a** (164.6 mg, 1.01 mmol) was added to the solution, and the mixture was stirred for 30 min, acidified (acetic acid 1 ml and water 15 ml), and extracted with dichloromethane (5 ml). The organic layer was concentrated, and distilled by Kugelrohr to give a mixture of **2g** and **2h** (77:23 by capillary glc). Yield 253.2 mg (96%). Purity (as a mixture of **2g** and **2h**) 99%, ot. 115–150°C/1.2 mmHg. Found: C, 55.59; H, 7.77%. Calcd for $C_{12}H_{20}S_3$: C, 55.33; H, 7.74%.

2g. ^{1}H NMR ($CDCl_3$) δ 0.772 (6H, t, J = 7.4 Hz, $2CH_3$), 1.124 (1H, t, J = 8.8 Hz, SH), 1.404 (4H, q, J = 7.4 Hz, $2CH_2$), 2.196 (3H, dd, J = 1.0, 0.4 Hz, CH_3), 2.542 (2H, d, J = 9.0 Hz, $C\underline{H}_2SH$), 2.910 (2H, s, SCH_2), and 6.81–6.92 ppm (2H, m, 2 CH). GC-MS m/z (%) 260 (59, M), 143 (12, $Me(C_4H_2S)SCH_2^+$), 130 (100), 129 (31, $Me(C_4H_2S)S^+$), 97 (35, $MeC_4H_2S^+$), 85 (21).

2h. ^{1}H NMR ($CDCl_3$) δ 2.306 (3H, s, CH_3), 2.812 (2H, s, SCH_2), and 7.210 ppm (1H, d, J = 6.0 Hz, H-5 in thiophene). GC-MS m/z (%) 260 (52, M), 143 (12, $Me(C_4H_2S)SCH_2^+$), 130 (100), 129 (35, $Me(C_4H_2S)S^+$), 97 (46, $MeC_4H_2S^+$), 85 (28), 69 (24).

Reaction with 2-Lithiobenzo[b]thiophene **3c**. Benzo[b]thiophene **4c** (211 mg, 1.57 mmol) was lithiated with BuLi (1.63 mmol) at room temperature for 30 min under argon. Dithiolane **1a** (260 mg, 1.60 mmol) was added to the solution by means of syringe, and the mixture was stirred at room temperature for 30 min. The mixture was mixed with acetic acid (1.5 ml), water (20 ml), and dichloromethane (5 ml). The organic layer was distilled by Kugelrohr to give **2f**, yield 413 mg (87%), purity 99% (glc), ot. 160–190°C/0.8 mmHg. Found: C, 60.75; H, 6.73%. Calcd for $C_{15}H_{20}S_3$: C, 60.76; H, 6.80%. IR (KBr) ν 2966 (s), 2928 (m), 2574 (vw, S—H), 1456 (m), 1425 (m), 745 (m), and 725 cm^{-1} (m). ^{1}H NMR ($CDCl_3$) δ 0.778 (6H, t, J = 7.4 Hz, $2CH_3$), 1.156 (1H, t, J = 8.8 Hz, SH), 1.416 (4H, q, J = 7.4 Hz, $2CH_2$), 2.548 (2H, d, J = 8.8 Hz, $C\underline{H}_2SH$), 3.042 (2H, s, CH_2S), 7.20–7.36 (3H, m, CH), and 7.58–7.74 ppm (2H, m, CH). ^{13}C NMR ($CDCl_3$) δ 7.60 ($2CH_3$), 26.36 ($2CH_2$), 30.42 (CH_2SH), 41.00 (C), 44.18 (CH_2S), 121.78 (CH), 122.88 (CH), 124.24 (CH), 124.42 (CH), 127.42 (CH), 138.36 (C), 139.78 (C), and 141.38 ppm (C). MS m/z (%) 296 (44, M), 168 (10), 167 (15), 166 (100), 165 (24, $C_8H_5S_2^+$), 134 (13), 121 (26), 97 (15).

Reaction of Naphthalene-1,8-disulfide **5** *with* **3a**. To a solution of **3a** prepared from **4a** (121 mg, 1.2 mmol) and BuLi (1.0 mmol) in THF (2.5 ml), a solution of naphthalene-1,8-disulfide **5** (96 mg, 0.50 mmol) in THF (2.5 ml) was added and the mixture was stirred at room temperature for 0.5 h. After addition of 1N HCl (10 ml), the mixture was extracted with CH_2Cl_2 (5 ml × 3 times), and the organic layer was concentrated under reduced pressure. The residue was let stand at room temperature under reduced pressure to give the ring opened products **6** of constant weight 144 mg (yield 99%) in a reasonable purity. Found: C, 62.49; H, 4.24%. Calcd for $C_{15}H_{12}S_3$: C, 62.46; H, 4.19%. IR (KBr) ν 2532 (w, SH), 1549 (s), 1437 (m), 1361 (m), 1319 (m), 1214 (s), 1160 (m), 1065 (m), 982 (m), 953 (m), 868 (m), 812 (s), 758 (s), 717 (m), and 507 cm^{-1} (m). ^{1}H NMR ($CDCl_3$) δ 2.390 (3H, d, J = 0.7 Hz, CH_3), 4.254 (1H, d, J = 0.7 Hz, SH), 6.626 (1H, dq, J = 3.5 and 1.0 Hz), and 7.08–7.70 ppm (7H, m). ^{13}C NMR ($CDCl_3$) δ 15.70 (CH_3), 125.60 (CH), 125.76 (CH), 125.86 (CH), 127.42 (CH), 129.30 (CH), 130.06 (C), 131.12 (C), 131.32 (CH), 131.70 (C), 132.24 (CH), 134.34 (CH), 135.64 (C), 136.10 (C), and 145.22 ppm (C). MS m/z (%) 288 (6, M), 286 (30), 255 (10), 254 (24), 252 (16), 192 (10), 191 (14, $M(C_4H_2S)Me$), 190 (100), 129 (44, $S(C_4H_2S)Me$), 114 (20), 95 (10), 85 (10), 69 (16).

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