A Convenient Preparation of 1,3-Dithiole-2-thione and 1,3-Diselenole-2-selone Derivatives

K. Takimiya, A. Morikami, T. Otsubo*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739, Japan

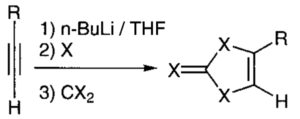
Fax +81-824-22-7191; E-mail otsubo@ipc.hiroshima-u.ac.jp

Received 25 December 1996

Abstract: A convenient one-pot preparation of 1,3-dithiole-2-thiones and 1,3-diselenole-2-selones substituted with phenyl, alkyl, alkylthio, hydroxymethyl, and formyl groups was accomplished from readily available acetylenes in good to excellent yields.

In the synthesis of tetrathiafulvalene (TTF) derivatives, the most prevailing family of π-electron donors for organic metals and superconductors,[1] the key intermediate is 1,3-dithiole-2-thiones, which can be readily converted into the TTF derivatives by desulfurization coupling with trivalent phosphorus reagents or by carbenoid coupling after conversion to the dithiolium salts.[2] Recent interests in TTF chemistry have been directed towards more sophisticated multi-TTF systems[3] and 1,3-dithiole-based new materials,[4] which might serve as building blocks in supramolecular chemistry. For the construction of such compounds, it is of great importance to easily prepare 1,3-dithiole-2-thiones with various functional groups. However, only a limited number of the intermediates are relatively accessible.[5] In addition, there have been so far few useful synthetic methods of 1,3-diselenole-2-selones producing tetraselenafulvalene (TSF) derivatives, even though the TSF donors are more interesting because the substitution of sulfur atoms in the TTF skeleton with selenium atoms often makes a marked improvement in the conductive properties of the charge-transfer complexes.[6]

For these reasons, we have searched for a general and easy synthetic method applicable to both 1,3-dithiole-2-thiones and 1,3-diselenole-2-selones. Mayer and co-workers in 1964 reported a simple synthesis of 1,3-dithiole-2-thione by cyclization reaction of sodium acetylides with sulfur and carbon disulfide in liquid ammonia.[7] The yield was, however, very low (25%), though the phenyl derivative was obtained in 65 % yield. No additional examples have been reported, but later this method was applied to the preparation of 1,3-diselenole-2-selone with low yield (15-25 %).[8] We thought that this reaction, in spite of the disadvantages of its low yield and laborious procedure using liquid ammonia, had significant synthetic potential, and reexamined it in detail. As a result, it has turned out that substantial experimental modifications to the reaction conditions can be effectively accomplished and the best one is as follows. Trimethylsilylacetylene (**1a**) with n-BuLi in THF at -78 °C was converted into lithium trimethylsilylacetylide, which was subsequently reacted with sulfur at 0 °C for 2 h and then with carbon disulfide at -90 °C for 3 min to give 1,3-dithiole-2-thione (**2a**) in 82 % isolated yield. A similar reaction using a combination of selenium and carbon diselenide instead of sulfur and carbon disulfide also gave 1,3-diselenole-2-selone (**3a**) in excellent yield (94 %). It is supposed that spontaneous removal of the silyl group was induced by lithium hydroxide produced upon quenching the reaction by addition of water.



1a R = TMS
1b R = Ph
1c R = SMe
1d R = CH$_2$OTHP
1e R = Hexyl
1f R = CH(OEt)$_2$

2a X = S, R = H
2b X = S, R = Ph
2c X = S, R = SMe
2d X = S, R = CH$_2$OTHP
2e X = S, R = Hexyl
2f X = S, R = CH(OEt)$_2$

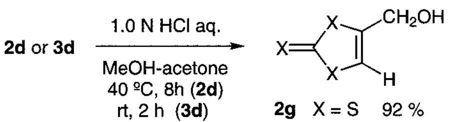
3a X = Se, R = H
3b X = Se, R = Ph
3c X = Se, R = SMe
3d X = Se, R = CH$_2$OTHP
3e X = Se, R = Hexyl
3f X = Se, R = CH(OEt)$_2$

Scheme 1

As indicated in Scheme 1, nearly all the acetylenes with a wide variety of substituent groups which are inert to n-BuLi at -78 °C gave the corresponding heterocyclic products (**2**) and (**3**) in good to excellent isolated yields. Table 1 summarizes the results of the optimized yields.[9] The addition of tetramethylethylenediamine (TMEDA) is usually effective for enhancing the yields, especially for the selenium cases. All the selenium heterocycles (**3**) were thus obtained in high yields (entries 7-12). In contrast, the yields of the sulfur heterocycles (**2**) fairly depend on the substituent groups. The reactions of phenylacetylene (entry 2), methylthioacetylene (entry 3),[10] and 1-octyne (entry 5) similarly proceeded in high yields, while THP-protected propargyl alcohol[11] and propargylaldehyde diethylacetal gave very low yields (15-20 %) of the desired heterocycles. In the best cases where the acetylides were treated with sulfur at a lower temperature (-30~-40 °C) in the absence of TMEDA, **2d** was obtained in 58 % yield (entry 4) and **2f** in 34 % yield (entry 6). On treatment with dil. hydrochloric acid, the dihydropyranyloxymethyl compounds **2d** and **3d** and the diethoxymethyl compounds **2f** and **3f** were conveniently deprotected to the hydroxymethyl ones **2g**[12a] and **3g** (Scheme 2) and the formyl ones **2h**[12] and **3h** (Scheme 3), respectively,[13] which are important intermediates for the synthesis of functionalized TTF systems.

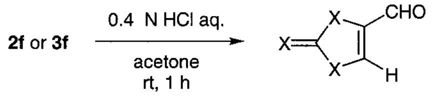
Table 1. Preparation of 1,3-dithiole-2-thiones (**2**) and 1,3-diselenole-2-selones (**3**).

Entry	Acetylene	X	Additive	Product	Yield / %
1	**1a**	S	none	**2a**	82
2	**1b**	S	TMEDA	**2b**	83
3	**1c**	S	TMEDA	**2c**	75
4	**1d**	S	none	**2d**	58
5	**1e**	S	TMEDA	**2e**	72
6	**1f**	S	none	**2f**	34
7	**1a**	Se	TMEDA	**3a**	94
8	**1b**	Se	TMEDA	**3b**	quant.
9	**1c**	Se	TMEDA	**3c**	92
10	**1d**	Se	TMEDA	**3d**	91
11	**1e**	Se	TMEDA	**3e**	81
12	**1f**	Se	TMEDA	**3f**	85



2g X = S 92 %
3g X = Se 83 %

Schemes 2



2h X = S 98 %
3h X = Se quant.

Scheme 3

In summary, because of its high yield, versatility, and easy operation, the present one-pot reaction provides an efficient and practical synthetic tool for various substituted 1,3-dithiole-2-thiones and 1,3-diselenole-2-selones. Especially, for the preparation of 1,3-diselenole-2-selones, we believe this would be the best one among the reported methods.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 06243150 and 08740498) from the Ministry of Education, Science, Sports and Culture of Japan. One of the authors (K. T.) is also indebted to a financial support from Yazaki Memorial Foundation for Science and Technology.

Reference and Notes

(1) For a comprehensive review, see: Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. -H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory*; Prentice Hall: New Jersey, 1992.

(2) Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Reports* **1987**, *7*, 155.

(3) For recent topics on multi-TTF systems, see: (a) JØrgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41. (b) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439. (c) Otsubo, T.; Aso, Y.; Takimiya, K.; *ibid.* **1996**, *8*, 203.

(4) For applications of the 1,3-dithiole units to new materials, see: Hansen, T. K.; Becher, J. *Adv. Mater.* **1993**, *5*, 288.

(5) Svenstrup, N.; Becher, J. *Synthesis* **1995**, 215.

(6) Cowan, D.; Kini, A. *The Chemistry of Organic Selenium and Tellurium*, Patai, S., Ed.; John Wiley & Sons: New York, 1987; Vol. 2, Chapter 12.

(7) (a) Mayer, R.; Gebhardt, B; Fabian, J.; Müller, A. K. *Angew. Chem.* **1964**, *76*, 143. (b) Mayer, R.; Gebhardt, B. *Chem. Ber.* **1964**, *97*, 1298. (c) Mayer, R.; Hunger, B.; Prousa, R.; Müller, A.-K. *J. Prakt. Chem.* **1967**, *35*, 294.

(8) (a) Engler, E. M.; Patel, V. V. *J. Am. Chem. Soc.* **1974**, *96*, 7376. (b) Engler, E. M.; Patel, V. V. *J. Org. Chem.* **1975**, *40*, 387. (c) Lyubovskaya, R. N.; Lipshan, Y. D.; Krasochka, O. N.; Atovmyan. L. O. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1976**, 179; *Chem. Abstr.* **1976**, *84*, 135562q. (d) Poleschner, H.; Fanghänel, E. *J. Prakt. Chem.* **1982**, *324*, 691.

(9) *Typical procedure for the preparation of 1,3-dithiole-2-thiones and 1,3-diselenole-2-selones.* To a mixture of mono-substituted acetylene (**1**) (2 mmol) and tetramethylethylenediamine (0.61 mL, 4 mmol) in 10 mL of dry THF cooled at -78 °C was added a hexane solution of n-BuLi (1.6 N, 1.3 mL, 2.08 mmol), and the resulting solution was stirred for 30 min at the same temperature. To the resulting lithium acetylide solution, sulfur (64 mg, 2 mmol) was added in one portion, and the reaction mixture was allowed to warm to 0 °C during the period of 2 h and stirred for additional 2 h at 0 °C. Then the mixture was cooled again to -90 °C, and carbon disulfide (0.8 mL, 13 mmol) was added. The mixture was stirred for 3 min, then quenched by the addition of 20 mL of water containing THF (1:1, v/v), and allowed to warm to room temperature. The reaction mixture was extracted with dichloromethane (3 x 20 mL), and the extracts were washed with water (60 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent and a subsequent short column chromatography on silica-gel eluted with CH_2Cl_2 gave crude 1,3-dithiole-2-thione (**2**), which was subjected to further purification with gel permeation chromatography or recrystallization.

All the new compounds were characterized with ^{1}H-NMR ($CDCl_3$), ^{13}C-NMR ($CDCl_3$), IR (KBr), MS (EI, 70 eV), and C and H elemental analyses within an error of 0.3%. Physical and spectroscopic data of **2a**: yellow plates from hexane; mp 48.0-48.5 °C (Lit.[7b] 48.5 °C); ^{1}H-NMR δ 7.13 (s, CH); ^{13}C-NMR δ 129.2 (olefinic) and 213.3 (C=S); IR 1046 cm^{-1} (C=S); MS *m/z* 134 (M^+). **2b**: yellow plates from chloroform.; mp 120.0-120.5 °C (Lit.[7c] 118-119 °C); ^{1}H-NMR δ 7.11 (s, 1H, CH) and 7.41 (s, 5H, Ph); ^{13}C-NMR δ 121.9, 126.4, 129.3, 129.6, 130.9 (olefinic and Ph), 146.2 (olefinic), and 212.2 (C=S); IR 1059 cm^{-1} (C=S); MS *m/z* 210 (M^+). **2c**: yellow prisms from hexane; mp 73.5-74.5 °C; ^{1}H-NMR δ 2.48 (s, 3H, CH_3) and 6.84 (s, 1H, CH); ^{13}C-NMR δ 19.7 (CH_3), 127.0 (CH, olefinic), 138.5 (olefinic) and 213.3 (C=S); IR 1059 cm^{-1} (C=S); MS *m/z* 180 (M^+). **2d**: yellow oil; ^{1}H-NMR δ 1.65 (m, 6H, CH_2), 3.60 (m, 2H, CH_2), 4.52 (dd, J = 1.0 and 2.6 Hz, 2H, CH_2), 4.70 (m, 1H, CH) and 6.89 (t, J = 1.0 Hz, 1H, CH); ^{13}C-NMR δ 18.7, 25.0, 29.9 (CH_2), 62.0 (CH_2), 63.2 (CH_2), 97.5 (CH), 124.7 (CH, olefinic), 144.5 (olefinic), and 213.5 (C=S); IR (neat) 1123 (C-O-C), 1063 (C=S), and 1032 cm^{-1} (C-O-C); MS *m/z* 248 (M^+). **2e**: yellow oil; ^{1}H-NMR δ 0.89 (t, J = 6.8 Hz, 3H, CH_3), 1.28-1.38 (m, 6H, CH_2), 1.61 (m, 2H, CH_2), 2.62 (dt, J = 1.2 and 8.0 Hz, 2H, CH_2) and 6.66 (t, J = 1.2 Hz, 1H, CH); ^{13}C-NMR δ 14.0 (CH_3), 22.5, 28.5, 29.8, 31.3 (x 2) (CH_2), 122.1 (CH, olefinic), 148.7 (olefinic), and 213.8 (C=S); IR (neat) 1059 cm^{-1} (C=S); MS *m/z* 218 (M^+). **2f**: yellow oil; ^{1}H-NMR δ 1.25 (t, J = 7.0 Hz, 6H, CH_3), 3.61 (q, J = 7.0 Hz, 2H, CH_2), 3.68 (q, J = 7.0 Hz, 2H, CH_2), 5.40 (d, J = 1.0 Hz, 1H, CH), and 7.05 (d, J = 1.0 Hz, 1H, CH); ^{13}C-NMR δ 14.9 (CH_3), 61.6 (CH_2), 96.9 (CH), 125.5 (CH, olefinic), 145.9 (olefinic), and 213.7 (C=S); IR (neat) 1132 (C-O-C) and 1062 cm^{-1} (C=S); MS *m/z* 236 (M^+).

Physical and spectroscopic data of **3a**: red plates from benzene-hexane; mp 115.0-116.0 °C (Lit.[8b] 113.5-114 °C); ^{1}H-NMR δ 7.98 (s, CH); ^{13}C-NMR d 139.6 (olefinic) and 207.8 (C=Se); IR 889 cm^{-1} (C=Se); MS *m/z* 278 (^{80}Se, M^+) with an isotropic pattern of three seleniums. **3b**: red plates from chloroform; mp 121.0-122.0 °C (Lit.[8d] 121 °C); ^{1}H-NMR δ 7.40 (m, 5H, Ph) and 7.92 (s, 1H, CH); ^{13}C-NMR δ 127.2, 129.3, 129.4, 132.1, 134.1 (olefinic and Ph), 157.5 (olefinic), and 206.9 (C=Se); IR 905 cm^{-1} (C=Se); MS *m/z* 354 (^{80}Se, M^+). **3c**: black plates from benzene-hexane; mp 86.5-87.0 °C; ^{1}H-NMR δ 2.52 (s, 3H, CH_3) and 7.68 (s, 1H, CH); ^{13}C-NMR δ 20.9 (CH_3), 136.0 (CH, olefinic), 147.8 (olefinic), and 208.3 (C=Se); IR 907 cm^{-1} (C=Se); MS *m/z* 324 (^{80}Se, M^+).

3d: red oil; ^{1}H-NMR δ 1.65 (m, 6H, CH_2), 3.50-3.80 (m, 2H, CH_2), 4.60 (dd, J = 1.0 and 2.5 Hz, 2H, CH_2), 4.71 (m, 1H, CH), and 7.68 (t, J = 1.0 Hz, 1H, CH); ^{13}C-NMR δ 18.8, 25.1, 30.0 (CH_2), 62.1 (CH_2), 66.3 (CH), 97.5 (CH), 133.2 (CH, olefinic), 156.6 (olefinic), and 208.5 (C=Se); IR (neat) 1121, 1028 (C-O-C), and 899 cm^{-1} (C=Se); MS *m/z* 392 (^{80}Se, M^+). **3e**: red oil; ^{1}H-NMR δ 0.89 (t, J = 6.8 Hz, 3H, CH_3), 1.28-1.37 (m, 6H, CH_2), 1.61 (m, 2H, CH_2), 2.74 (dt, J = 1.2 and 7.4 Hz, 2H, CH_2), and 7.52 (t, J = 1.2 Hz, 1H, CH); ^{13}C-NMR δ 13.8 (CH_3), 22.3, 28.3, 30.6, 31.1, 34.4 (CH_2), 131.6 (CH, olefinic), 160.2 (olefinic), and 208.3 (C=Se); IR (neat) 905 cm^{-1} (C=Se); MS *m/z* 362 (^{80}Se, M^+). **3f**: red oil; ^{1}H-NMR δ 1.23 (t, J = 7.0 Hz, 6H, CH_3), 3.62 (q, J = 7.0 Hz, 2H, CH_2), 3.64 (q, J = 7.0 Hz, 2H, CH_2), 5.39 (d, J = 1.3 Hz, 1H, CH), and 7.82 (d, J = 1.3 Hz, 1H, CH); ^{13}C-NMR δ 15.1 (CH_3), 61.7 (CH_2), 99.3 (CH), 134.6 (CH, olefinic), 157.7 (olefinic), and 209.0 (C=Se); IR (neat) 1123, 1055 (C-O-C) and 905 cm^{-1} (C=Se); MS *m/z* 380 (^{80}Se, M^+).

(10) Brandsma, L.; Wijers, H. E.; Jonker, M. C. *Rec. Trav. Chem.* **1963**, *82*, 208.

(11) Earl, R. A.; Townsend, L. B. *Organic Synthesis Collective Vol. 7*, 335; John Wiley & Sons: New York, 1990.

(12) (a) Nozdryn, T.; Cousseau, J.; Gorgues, A.; Jubault, M.; Orduna, J.; Uriel, S.; Garín, J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1711. (b) Andreu, R.; Garín, J.; Orduna, J.; Savirón, M.; Cousseau, J.; Gorgues, A.; Morisson, V.; Nozdryn, T.; Becher, J.; Clausen, R. P.; Bryce, M. R.; Skabara, P. J.; Dehaen, W. *Tetrahedron Lett.* **1994**, *35*, 9243. (c) Clausen, R. P.; Becher, J. *Tetrahedron* **1996**, *52*,

3171.

(13) Physical and spectroscopic data of **2g**: yellow needles from benzene-hexane; mp 44.0-44.5 °C (Lit.[12a] 43-44 °C); ^{1}H-NMR δ 2.50 (t, J = 5.8 Hz, 1H, OH), 4.61 (dd, J = 1.2 and 5.8 Hz, 2H, CH_2), and 6.96 (t, J = 1.2 Hz, 1H, CH); ^{13}C-NMR δ 60.2 (CH_2), 124.0 (CH, olefinic), 147.3 (olefinic), and 213.7 (C=S); IR 3600-3100 (OH) and 1063 cm^{-1} (C=S); MS *m/z* 164 (M^+). **2h**: yellow plates from benzene-hexane; mp 86.3-87.0 °C (Lit.[12a] 87 °C); ^{1}H-NMR δ 7.96 (s, 1H, CH) and 9.52 (s, 1H, CHO); ^{13}C-NMR δ 142.8 (CH), 146.5 (olefinic), 178.8 (CHO), and 209.9 (C=S); IR 1665 (C=O) and 1082 cm^{-1} (C=S); MS *m/z* 162 (M^+). **3g**: red needles from benzene-hexane; mp 72.5-73.0 °C; ^{1}H-NMR δ 2.23 (t, J = 6.0 Hz, 1H, OH), 4.70 (dd, J = 1.2 and 6.0 Hz, 2H, CH_2), and 7.73 (t, J = 1.2 Hz, 1H, CH); ^{13}C-NMR δ 63.2 (CH_2), 132.3 (CH), 159.0 (olefinic), and 207.9 (C=Se); IR 3700-3100 (OH) and 907 cm^{-1}(C=Se); MS *m/z* 308 (^{80}Se, M^+). **3h**: purple needles from benzene-hexane; mp 121.8-122.2 °C; ^{1}H-NMR δ 8.96 (s, 1H, CH) and 9.58 (s, 1H, CHO); ^{13}C-NMR δ 154.4 (CH), 158.1 (olefinic), 180.7 (CHO), and 203.0 (C=Se); IR 1673 (C=O) and 907 cm^{-1} (C=Se). MS *m/z* 306 (^{80}Se, M^+).