  Bull. Chem. Soc. Jpn., 60, 365—368 (1987)

Syntheses of Bis(vinylenedithio)tetrathiafulvalene and Bis(methylvinylenedithio)tetrathiafulvalene

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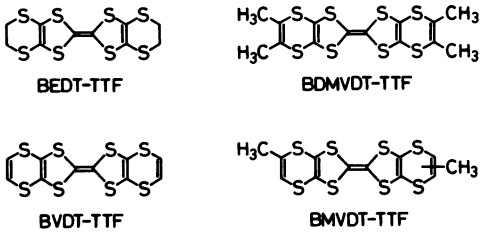
(Received July 28, 1986)

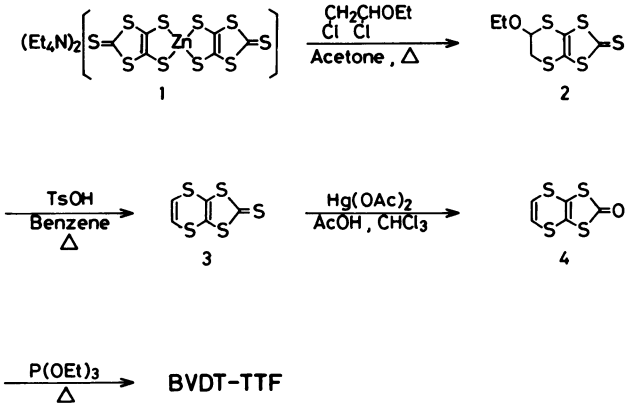
Bis(vinylenedithio)tetrathiafulvalene (BVDT-TTF) and bis(methylvinylenedithio)tetrathiafulvalene (BMVDT-TTF) were synthesized as attractive donor molecules for highly conductive organic salts. These molecules have analogous structures to BEDT-TTF, but are expected to possess more planar structures. They have higher oxidation potentials than BEDT-TTF. The synthetic method of BVDT-TTF by using a phase-transfer catalyst was also studied.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is known to give superconductive organic salts.[1,2] BEDT-TTF salts possess a two-dimensional electrical-conductivity character due to the presence of eight sulfur atoms in the donor molecule. Since BEDT-TTF has two ethylene units at both sides of the molecule, it is nonplanar.[3] One of the important factors for donor and acceptor molecules which give highly conductive salts is their planar structures. A replacement of the ethylene units of BEDT-TTF with carbon–carbon double bonds would give an attractive donor molecule since it has an analogous structure to BEDT-TTF and is expected to possess a more planar structure. The IBM group has reported the syntheses of bis(vinylenedithio)tetrathiafulvalene (BVDT-TTF) and bis(dimethylvinylenedithio)tetrathiafulvalene (BDMVDT-TTF) without a detailed description of the synthetic procedures.[4] They synthesized these donor molecules, starting from a reaction of 1,3,4,6-tetrathiapentalene-2,5-dione with a phase-transfer catalyst and Na_2CO_3. We also synthesized BDMVDT-TTF[5] by a different route. We have now synthesized BVDT-TTF and bis(methylvinylenedithio)tetrathiafulvalene (BMVDT-TTF) by different routes from those of the IBM group. The IBM method is assumed to be broadly applicable to the syntheses of the related donor molecules, and deserves to be studied in detail. We synthesized 4,5-(vinylenedithio)-1,3-dithiol-2-one, which is a precursor to BVDT-TTF, by the method reported by the IBM group. Since no detailed synthetic procedure has been disclosed for this method, and some researchers claim that this method is difficult,[6] it will be worth describing the synthetic procedures. We found that our method is superior to the IBM method.



Results and Discussion

Synthesis of BVDT-TTF. BVDT-TTF was synthesized by four reaction steps (Scheme 1). The synthesis of the starting material, $(Et_4N)_2[Zn(dmit)_2]$ (**1**),[7] was made by the reported method.[8] The synthesis of 4,5-(ethoxyethylenedithio)-1,3-dithiole-2-thione (**2**) was made by a reaction of **1** with 1,2-dichloroethyl ethyl ether in refluxing acetone. A dilution method is crucial for the synthesis of **2**, since its yield was poor without the dilution method. An elimination reaction of ethanol from **2** was made by refluxing a benzene solution of **2** and anhydrous *p*-toluenesulfonic acid to give 4,5-(vinylenedithio)-1,3-dithiole-2-thione (**3**). Since the coupling reaction of **3** with triethyl phosphite gave BVDT-TTF in low yield, **3** was converted to 4,5-(vinylenedithio)-1,3-dithiol-2-



Scheme 1.

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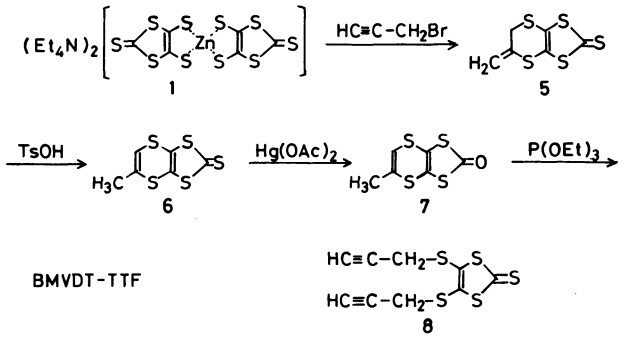
one (**4**) by treating with mercury(II) acetate. The coupling reaction of **4** was made by heating it in neat triethyl phosphite, and BVDT-TTF was obtained as red needles. The cyclic voltammetry of BVDT-TTF in THF (0.1 M n-Bu_4NClO_4, Pt electrode, 20 mV s^{-1}) exhibited one wave: $E_{1/2}$=0.83 V vs SCE. This value was higher than those of the BEDT-TTF observed in THF ($E_{1/2}(1)$=0.69 V, $E_{1/2}(2)$=0.82 V vs SCE).

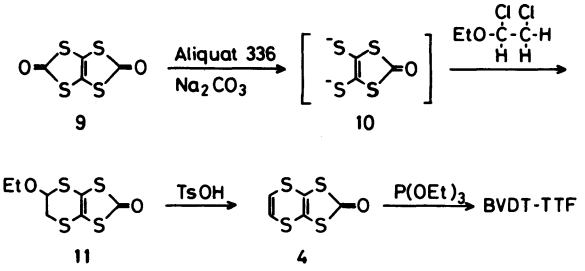
Synthesis of BMVDT-TTF. BMVDT-TTF was also synthesized by a four step reaction (Scheme 2). Reaction of **1** with propargyl bromide in refluxing acetone gave 4,5-(2-methylene-1,2-ethanediyldithio)-1,3-dithiole-2-thione (**5**). The dilution method is also crucial for this reaction. Without this method, two successive substitution reactions occurred to give 4,5-bis(propargylthio)-1,3-dithiole-2-thione (**8**) as the main product (judging from the mass and IR spectra). Product **5** was isomerized to 4,5-(methylvinylenedithio)-1,3-dithiole-2-thione (**6**) by treating **5** with p-toluenesulfonic acid monohydrate in toluene. Since the coupling reaction of **6** with neat triethyl phosphite gave BMVDT-TTF in low yield (16%), **6** was converted to 4,5-(methylvinylenedithio)-1,3-dithiol-2-one (**7**) by treating with mercury(II) acetate. The coupling reaction of **7** with neat triethyl phosphite gave BMVDT-TTF as light-yellow needles. The cyclic voltammetry of BMVDT-TTF in THF also gave one redox wave ($E_{1/2}$=0.80 V vs. SCE). This value was also higher than those of BEDT-TTF.

Synthesis of BVDT-TTF by Using Phase-Transfer Catalyst. Since the IBM group has disclosed no detailed synthetic procedure for the syntheses of BVDT-TTF and the related donor molecules,[4] we studied the synthetic conditions of BVDT-TTF by their method. The reaction route is shown in Scheme 3. The synthesis of 1,3,4,6-tetrathiapentalene-2,5-dione (**9**) was made by the reported method.[9] A benzene/water solution containing **9**, Aliquat 336,[10] and sodium carbonate was stirred at 40—45 °C to give 2-oxo-1,3-dithiole-4,5-dithiolate (**10**) in benzene phase. Then, the aqueous phase was eliminated by a syringe. Without the elimination of the aqueous phase, another carbonyl group also reacted to give tetrathiolate. The reaction of **10** with 1,2-dichloroethyl ethyl ether gave 4,5-(ethoxyethylenedithio)-1,3-dithiol-2-one (**11**). The elimination of ethanol from **11** was made by treating with p-toluenesulfonic acid in chlorobenzene to give **4**, which is a precursor to BVDT-TTF.

We have studied two different synthetic routes of BVDT-TTF (Schemes 1 and 3). Comparing these methods, the method shown in Scheme 1 is better than that in Scheme 3 from the following reasons. (1) The starting material, $(Et_4N)_2[Zn(dmit)_2]$,[7] in Scheme 1 can be obtained on a large scale (about 150 g) in one day. Therefore, the succeeding synthesis can be made on a large scale. On the other hand, a large-scale synthesis of **9** is not only difficult, but its synthesis requires several days. Although **9** can be commercially obtained, it is expensive. Furthermore, **9** sensitizes and produces skin rashes on some individuals. (2) All of the reaction products in Scheme 1 can be easily purified by recrystallization or chromatography. On the other hand, the product in Scheme 3 must be purified by column chromatography, followed by recrystallization, mainly due to the contamination of Aliquat 336. Thus, a much longer time is required for the purification. The loss of the product during these procedures is also a serious problem.



Scheme 2.



Scheme 3.

Experimental

The reaction was made under a nitrogen atmosphere, except for the syntheses of **4** and **7**. In the following reactions, second crops of **2**, **3**, **4**, BVDT-TTF, **5**, **6**, **7**, and BMVDT-TTF could be obtained by concentrating the mother solutions of the recrystallizations.

4,5-(Ethoxyethylenedithio)-1,3-dithiole-2-thione (2). A two-liter flask containing 1.7 l of acetone was equipped with two dropping funnels. The funnels contained an acetone solution (200 ml) of **1** (25 g) and an acetone solution (100 ml) of 1,2-dichloroethyl ethyl ether (10 g), respectively. After refluxing the acetone in the flask, the acetone solutions of **1** and 1,2-dichloroethyl ethyl ether were simultaneously dropped into the flask with vigorous stirring for a 3-h period; the solution was then refluxed for another 21 h. After cooling to room temperature, an orange precipitate was filtered off, and the acetone in the filtrate was evaporated. The residue was extracted with benzene, washed with water, dried over Na_2SO_4, recrystallized from acetonitrile, and then from the mixed solvent of hexane and

chloroform (2:1) to give yellowish-brown needles of **2** (9.3 g, 50% yield based on **1**). Mp 108 °C. Found: C, 2.89; H, 31.19; S, 59.78%. Calcd for $C_7H_8OS_5$: C, 3.00; H, 31.32; S, 59.72%. MS *m/z* 268 (M^+).

4,5-(Vinylenedithio)-1,3-dithiole-2-thione (3). The azeotropic distillation of 100 ml of benzene from the benzene solution (105 ml) of *p*-toluenesulfonic acid monohydrate ($TsOH \cdot H_2O$, 7.086 g) eliminated water in the solution. Benzene (895 ml) was added to the solution, and 100 ml of benzene was distilled again. After the benzene solution of TsOH was refluxed, a benzene solution (200 ml) of **2** (5 g) was added from a dropping funnel. The solution was refluxed for 24 h with vigorous stirring. The reddish-yellow solution gradually became dark brown. After cooling to room temperature, the solution was washed with water, then with aqueous $NaHCO_3$, finally with water, and dried over Na_2SO_4. After evaporating the benzene, the residue was chromatographed on silica gel by using benzene as an eluent. The second red fraction contained **3**. It was chromatographed again on silica gel by using hexane and chloroform (2:1) to give pure **3** as yellow powders (890 mg, 23.7%). Mp 143—144 °C. Found: C, 27.09; H, 0.85; S, 71.91%. Calcd for $C_5H_2S_5$: C, 27.01; H, 0.85; S, 71.91%. MS *m/z* 222 (M^+). ^{1}H-NMR (CS_2) δ=6.63 (s).

4,5-(Vinylenedithio)-1,3-dithiol-2-one (4). To the chloroform solution (30 ml) of **3** (300 mg) was added 30 ml of acetic acid and 1.075 g of mercury(II) acetate; the solution was stirred for 20 min at room temperature. A white precipitate was filtered off, and the filtrate was washed with water, then with aqueous $NaHCO_3$, finally with water, and dried over Na_2SO_4. After evaporating the solvent, the residue was chromatographed on silica gel by using hexane and chloroform (1:1) as an eluent. The second orange fraction gave **4** as pale yellow powders (158 mg, 57%). Mp 99 °C. Found: C, 29.02; H, 0.91; S, 61.94%. Calcd for $C_5H_2OS_4$: C, 29.11; H, 0.91; S, 62.15%. MS *m/z* 206 (M^+). ^{1}H-NMR (CS_2) δ=6.59 (s).

Bis(vinylenedithio)tetrathiafulvalene (BVDT-TTF). Two hundred mg of **4** was added to 5 ml of triethyl phosphite (freshly distilled), and the solution was stirred for 2 h at 100—105 °C. After cooling to room temperature, the precipitate was collected, washed with methyl alcohol, and dried to give BVDT-TTF (132 mg, 72%). It was recrystallized from chloroform to give red needles of BVDT-TTF. Mp 227 °C (decomp). Found: C, 31.85; H, 1.02; S, 67.13%. Calcd for $C_{10}H_4S_8$: C, 31.56; H, 1.06; S, 67.38%. MS *m/z* 380 (M^+). ^{1}H-NMR (CS_2) δ=6.5 (s). λ_{max}^{THF} (log ε): 316 nm (3.83), 340 nm (3.84).

4,5-(2-Methylene-1,2-ethanediyldithio)-1,3-dithiole-2-thione (5). To the refluxing acetone (480 ml) was added (dropwise) an acetone solution (60 ml) of **1** (7.19 g) and acetone solution (30 ml) of propargyl bromide (2.38 g) simultaneously for a 8-h period. The solution was refluxed for another 18 h. The residue was filtered off, acetone was evaporated, and the oil was extracted with benzene. It was washed with water, dried over Na_2SO_4, and chromatographed on silica gel by using hexane and chloroform (4:1) as an eluent. The first yellow fraction contained **5** and **8**. It was chromatographed again on silica gel by using hexane and chloroform (6:1) as an eluent, and the first fraction gave **5** (802 mg, 17%). It was recrystallized from acetonitrile to give orange needles. Mp 114—116 °C. Found: C, 30.50; H, 1.61; S, 67.62%. Calcd for $C_6H_4S_5$: C, 30.49; H, 1.71; S, 67.81%. MS *m/z* 236 (M^+). ^{1}H-NMR (CS_2) δ=3.71 (2H, s), 5.29 (1H, s), 5.39 (1H, s).

4,5-(Methylvinylenedithio)-1,3-dithiole-2-thione (6). A toluene solution (50 ml) of **5** (250 mg) and *p*-toluenesulfonic acid monohydrate ($TsOH \cdot H_2O$, 0.4 g) was refluxed for 1 h, and TsOH was filtered off. The filtrate was washed with water and dried over Na_2SO_4. After evaporating the solvent, **6** was extracted with acetonitrile. It was recrystallized from acetonitrile to give **6** as orange needles (150 mg, 61%). Mp 103 °C. Found: C, 30.50; H, 1.61; S, 67.62%. Calcd for $C_6H_4S_5$: C, 30.49; H, 1.71; S, 67.81%. MS *m/z* 236 (M^+). ^{1}H-NMR (CS_2) δ=2.20 (3H, s), 6.18 (1H, s).

4,5-(Methylvinylenedithio)-1,3-dithiol-2-one (7). Mercury(II) acetate (0.34 g) and **6** (0.1 g) was added to the mixed solvent of chloroform (10 ml) and acetic acid (10 ml), and the solution was stirred for 15 min at room temperature. A white precipitate was filtered off and the filtrate was washed with water, then with aqueous $NaHCO_3$, finally with water, and dried over Na_2SO_4. It was chromatographed on silica gel by using the mixed solvent of hexane and chloroform (1:1). The first pale yellow fraction gave **7** (75 mg, 80%). Recrystallization from methanol gave analytically pure **7**. Mp 80.5—81 °C. Found: C, 32.64; H, 1.85; S, 58.17%. Calcd for $C_6H_4OS_4$: C, 32.71; H, 1.83; S, 58.20%. MS *m/z* 220 (M^+). ^{1}H-NMR (CS_2) δ=2.20 (3H, s), 6.12 (1H, s).

Bis(methylvinylenedithio)tetrathiafulvalene (BMVDT-TTF). To triethyl phosphite (8 ml, freshly distilled) was added 0.2 g of **7**, and the mixture was stirred for 2 h at 110 °C. The yellow product was collected (157 mg, 92%), washed with methyl alcohol, and recrystallized from chloroform to give BMVDT-TTF as yellow needles. Mp: gradually decomposes at around 204 °C. Found: C, 35.12; H, 2.11; S, 61.74%. Calcd for $C_{10}H_8S_8$: C, 35.27; H, 1.97; S, 62.76%. MS *m/z* 408 (M^+). ^{1}H-NMR (CS_2) δ=2.12 (3H, s), 6.03 (1H, s). λ_{max}^{THF} (log ε): 316 nm (3.69), 342 nm (3.69).

4,5-(Ethoxyethylenedithio)-1,3-dithiol-2-one (11). A four-necked flask containing **9** (624 mg, 3 mmol), Na_2CO_3 (636 mg, 6 mmol), benzene (40 ml), and water (40 ml) was equipped with two dropping funnels, which contained a benzene solution (40 ml) of Aliquat 336 (2.5 g) and benzene solution (40 ml) of 1,2-dichloroethyl ethyl ether (429 mg, 3 mmol), respectively. The solution in the reaction vessel was heated to 40—45 °C, and a benzene solution of Aliquat 336 was dropped for a 40-min period with vigorous stirring, then stirred for another 20 min. After cooling to room temperature, the aqueous phase was eliminated by a syringe. The dithiolate (**10**) was produced as a reddish benzene solution. The benzene solution of 1,2-dichloroethyl ethyl ether was then added dropwise to the above solution for a 30-min period with stirring at room temperature, and the solution was stirred for another 90 min at 40—45 °C. Filtration of the solution, followed by the evaporation of the solvent, gave dark red oil. It was extracted with benzene, washed with water, and dried over Na_2SO_4. After evaporating the benzene, the residue was chromatographed on silica gel by using a mixed solvent of hexane and chloroform (4:1) as an eluent. The second yellow fraction contained almost pure **11** as a reddish-yellow oil (454 mg, 60%). MS *m/z* 252 (M^+). It was difficult to purify **11** completely by repeated chromatographies due to the contamination of Aliquat 336. Thus, the crude product was

used directly in the next step of the reaction.

4,5-(Vinylenedithio)-1,3-dithiol-2-one (4) from 11. To *p*-toluenesulfonic acid monohydrate (5.538 g) was added the mixed solvent of benzene (80 ml) and chlorobenzene (80 ml). An azeotropic distillation of benzene eliminated any water in the solution. A chlorobenzene solution (10 ml) of **11** (1.157 g) was added to the above solution and was then refluxed for 4 h. After cooling to room temperature, the solution was washed with water and dried over Na_2SO_4. After evaporating chlorobenzene, the residue was chromatographed on silica gel by using a mixed solvent of hexane and chloroform (1 : 1) as an eluent. The first yellow fraction gave **4** (234 mg, 25%), which was recrystallized from acetonitrile to give light yellow needles. Mp 99.5—100.5 °C. Found: C, 29.19; H, 0.92; S, 61.26%. Calcd for $C_5H_2S_4O$: C, 29.11; H, 0.98; S, 62.15%. MS *m/z* 206 (M^+). ^{1}H-NMR (CS_2) δ=6.60.

The present work was partially supported by a Grant-in-Aid for Special Research Project on New Superconductive Materials (No. 59221012) from the Ministry of Education, Science and Culture.

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