



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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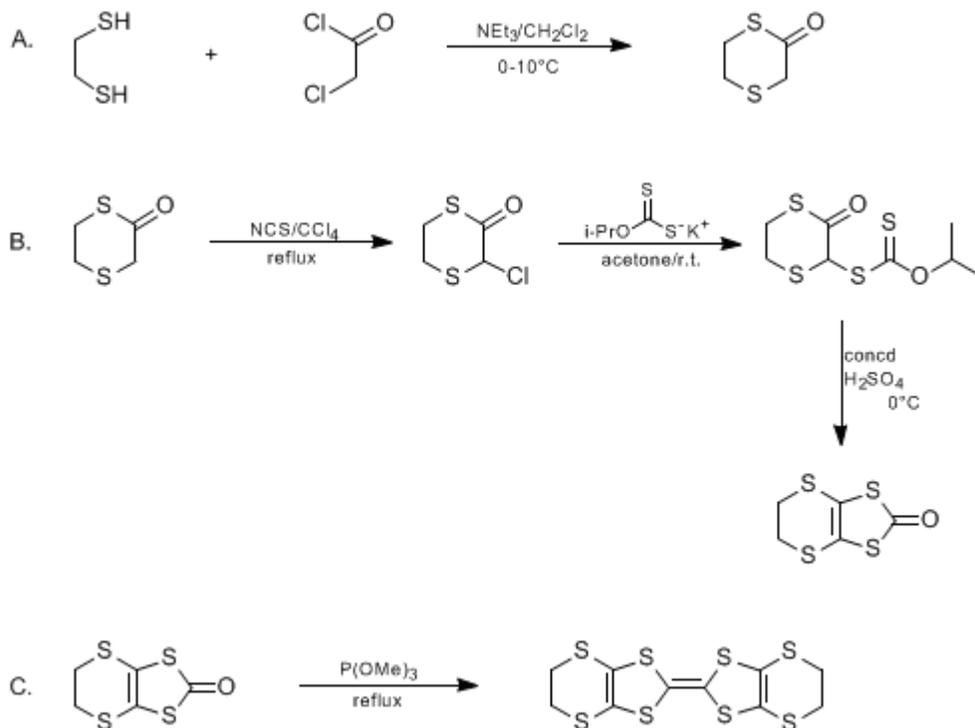
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2,2'-BI-5,6-DIHYDRO-1,3-DITHIOLO[4,5-b][1,4]DITHIINYLIDENE (BEDT-TTF)

[1,3-Dithiolo[4,5-b][1,4]dithiin, 2-(5,6-dihydro-1,3-dithiolo- [4,5-b][1,4]dithiin-2-ylidene)-5,6-dihydro-]



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1. Procedure

Caution! This preparation should be conducted in an efficient hood because of the obnoxious odor of 1,2-ethanedithiol.

A. *2-Oxo-1,4-dithiane*. A 4-L, four-necked, round-bottomed flask equipped with a mechanical stirrer, 500-mL pressure-equalizing dropping funnel, thermometer, and reflux condenser provided with a calcium chloride drying tube, is charged with 1 L of dichloromethane, 1,2-ethanedithiol (102 mL, 1.2 mol) (Note 1), and triethylamine (336 mL, 2.4 mol). The mixture is cooled while it is stirred in an ice-acetone bath to 0–10°C while a solution of chloroacetyl chloride (96 mL, 1.2 mol) (Note 2) in 400 mL of dichloromethane is added over a period of 1.5 hr, during which time a thick white precipitate of triethylamine hydrochloride is formed. After the addition is complete, stirring is continued for another 2 hr at ambient temperature. To the stirred mixture is added 500 mL of ice water. During the addition all the precipitated triethylamine hydrochloride is dissolved and a two-phase system is formed. The organic phase is washed with four 200-mL portions of water and dried over anhydrous magnesium sulfate (MgSO₄). The drying agent is removed by filtration, and the dichloromethane is evaporated using a rotary evaporator at ca. 13 mm. The residue is distilled at 0.7 mm using an oil bath with the temperature set at 120–130°C (Note 3) and 2-oxo-1,4-dithiane is distilled at 92–93°C; yield, 96 g (60%) (Note 4), (Note 5).

B. *3-Chloro-2-oxo-1,4-dithiane*. A 250-mL, round-bottomed flask, equipped with a magnetic stirring bar and a reflux condenser provided with a nitrogen bubbler, is flushed with nitrogen and charged with 150 mL of carbon tetrachloride (CCl₄), 2-oxo-1,4-dithiane (10.0 g, 0.075 mol), and N-chlorosuccinimide (11.0 g, 0.083 mol) (Note 6), (Note 7). The mixture is refluxed for 30 min. After cooling to 0°C the precipitated succinimide is removed by filtration and washed with 20 mL of CCl₄ (Note 8). The solution is filtered directly into a 1-L, conical flask equipped with a magnetic stirring bar, charged with a suspension of potassium O-(2-propyl) dithiocarbonate (13.1 g, 0.075 mol) (Note 9) in 300 mL of dry acetone, and stirred at ambient temperature for 0.5 hr. The precipitate is removed by filtration and the solvent is evaporated at ambient temperature using a rotary evaporator at ca. 13 mm. 2-Oxo-3-(2-propoxythiocarbonylthio)-1,4-dithiane is obtained in quantitative yield as a slightly brown oil and used in the following step without further purification (Note 10).

2-Oxo-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin. A 1-L conical flask, equipped with a magnetic stirring bar, is charged with 500 mL of concentrated sulfuric acid (H₂SO₄), and cooled to 0°C; 45 mL of ether is added dropwise. 2-Oxo-3-(2-propoxythiocarbonylthio)-1,4-dithiane is added in a thin stream during 10 min using an additional 5 mL of ether to complete the transfer. During the addition the sulfuric acid becomes dark. After 1.5 hr the reaction mixture is poured onto 3 kg of ice, at which time a sticky mass appears. The mixture is filtered by suction through a sintered glass funnel (D = 10 cm) charged with a layer of 2 cm of Celite. The Celite is washed with four 150-mL portions of water. A first crop is obtained by combining the water phase and leaving it for 5–7 days at room temperature. During this time the solution first becomes turbid and then clear, at which time 2-oxo-5,6-dihydro-1,3-dithiolo [4,5b][1,4]dithiin has separated as slightly yellow crystals. The water is removed by filtration, the product is washed with four 50-mL portions of water, and with two 20-mL portions of methanol, and dried under reduced pressure at ambient temperature.

The gummy mass isolated on the Celite is dissolved by washing with four 100-mL portions of dichloromethane. The organic phase is washed with three 100-mL portions of water and dried over anhydrous MgSO₄. The drying agent is removed by filtration and the solvent is evaporated using a rotary evaporator at ca. 13 mm. The residue is purified by filtration on silica gel (Note 11) with toluene. Toluene is evaporated using a rotary evaporator at ca. 13 mm. The residue is combined with the first crop and purified by recrystallization from absolute ethanol to yield 2-oxo-5,6-dihydro-1,3-dithiolo [4,5b][1,4]dithiin as white crystals (yield 7.8–9.4 g, 50–60% based on 2-oxo-1,4-dithiane); mp 126–127°C (Note 12).

C. *2,2'-Bi-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiinylidene(BEDT-TTF)*. A 250-mL, round-bottomed flask equipped with a magnetic stirring bar and reflux condenser provided with a nitrogen bubbler is charged with 100 mL of freshly distilled trimethyl phosphite and 2-oxo-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin (5.0 g, 0.024 mol). The solution is heated to reflux by immersing the flask in an oil bath preheated to 125°C (Note 13) for 2–3 hr. During this time bright orange-red crystals of product precipitate. The mixture is cooled to room temperature and the solid is filtered, and washed with four 20-mL portions of methanol and with four 20-mL portions of ether and dried under reduced pressure at ambient temperature to provide BEDT-TTF. Recrystallization from 300 mL of chlorobenzene affords 4.3 g (93%) of BEDT-TTF as bright red needles; mp 245–247°C (dec).

2. Notes

- 1,2-Ethanedithiol (99%) is available from Aldrich Chemical Company, Inc., and is used without further purification.
- Chloroacetyl chloride (98%) is available from Aldrich Chemical Company, Inc., and is used without further purification.
- The use of an electric heating mantle results in local overheating of the initially formed poly- or oligomeric products giving red, foul-smelling products instead. The product distills rather slowly (2–4 hr).
- The product was pure by NMR spectroscopy. ¹H NMR (CDCl₃/TMS) δ: 3.2 (m); ¹³C NMR (CDCl₃/TMS) δ: 25.82 (CH₂), 31.02 (CH₂), 35.25 (CH₂), 197.11 (C=O).
- 2-Oxo-1,4-dithiane can be stored for a long time at –20°C, at which temperature the product crystallizes.

6. *N*-Chlorosuccinimide (98%) is available from Aldrich Chemical Company, Inc., and is used without further purification.
7. The use of *N*-bromosuccinimide instead of *N*-chlorosuccinimide affords a dark, tarry mass.
8. 3-Chloro-2-oxo-1,4-dithiane can be obtained by removing the solvent at ambient temperature using a rotary evaporator at ca. 13 mm. The product was pure by NMR spectroscopy. ¹H NMR (CDCl₃/TMS) δ: 3.2 (m, 4 H, CH₂), 5.37 (s, 1 H, CH); ¹³C NMR (CDCl₃/TMS) δ: 24.52 (CH₂), 30.18 (CH₂), 61.91 (CH), 188.27 (C=O). The product becomes black in a few days, even when stored at -20°C.
9. Potassium O-(2-propyl) dithiocarbonate can be prepared in the following manner: With heating, 42 g (0.75 mol) of potassium hydroxide is dissolved in 400 mL of 2-propanol. The solution is then cooled in an ice bath, and the temperature is kept below 10°C while carbon disulfide (46 mL, 0.75 mol) is added dropwise with stirring. The potassium xanthate is collected by suction filtration and washed with four 100-mL portions of ether and dried under reduced pressure at ambient temperature; yield 111 g (85%).
10. The product was pure by NMR spectroscopy. ¹H NMR (CDCl₃/TMS) δ: 1.40 (d, 6 H, CH₃), 3.41 (m, 4 H, CH₂), 5.62 (s, 1 H, CH), 5.70 (sept, 1 H, CH); ¹³C NMR (CDCl₃/TMS) δ: 21.00 (CH₃), 27.70 (CH₂), 31.74 (CH₂), 54.17 (CH), 79.53 (CH), 191.58 (C=O), 207.71 (C=S).
11. Silicagel 60, 55 g, was used on a 5-cm column.
12. The product showed the following NMR data: ¹H NMR (CDCl₃/TMS) δ: 3.43 (s, 4 H, CH₂); ¹³C NMR (CDCl₃/TMS) δ: 31.08 (CH₂), 113.41 (C=C), 188.72 (C=O).
13. It is essential that the mixture be heated rapidly, otherwise the yield decreases dramatically.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

BEDT-TTF [Bis(ethylenedithio)tetrathiafulvalene] has been synthesized by a variety of methods, mostly by reduction of carbon disulfide with alkali metals,^{3,4,5} or electrochemically,⁶ followed by alkylation of the formed disodium 4,5-dimercapto-1,3-dithiole-2-thione with 1,2-dibromoethane,^{3,4,5} The thione is converted to 2-oxo-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin by oxidation with mercuric acetate.⁴ Finally coupling with triethyl phosphite,^{4,7,8} or direct coupling of the thione with triethyl phosphite^{5,9,10} or with triethyl phosphite under photochemical conditions¹¹ or with triethyl phosphite under high pressure¹² yields BEDT-TTF. Coupling has also been effected by alkylating the thione followed by electrochemical reduction of the formed 2-alkylthio-1,3-dithiolium salt.¹³ Pyrolysis then yields the final product.

BEDT-TTF was also obtained by selective ring opening of 1,3,4,6-tetrathiapentalen-2,6-dione and alkylation with 1,2-dibromoethane followed by coupling with triethyl phosphite.^{7,8}

The present procedure, which is based on those of Schumaker⁸ and Larsen and Lenoir,¹⁴ is simple and avoids the use of the troublesome and sometimes hazardous reduction of carbon disulfide with alkali metals. On several occasions a violent explosion has occurred in our laboratories during this reaction.

The present method gives high yields of BEDT-TTF in excellent purity. Actual investigation of super-conducting salts of BEDT-TTF show that BEDT-TTF made by the present route gives material of superior purity.¹⁵ Also by the present method BEDT-TTF is obtained from readily available starting materials.

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

silica gel

2-Oxo-3-(2-propoxythiocarbonylthio)-1,4-dithiane

2,2'-BI-5,6-DIHYDRO-1,3-DITHIOLO[4,5-b][1,4]DITHIINYLIDENE (BEDT-TTF)

2-oxo-5,6-dihydro-1,3-dithiolo[4,5b][1,4]dithiin

2,2'-Bi-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiinylidene(BEDT-TTF)

BEDT-TTF

Silicagel

BEDT-TTF [Bis(ethylenedithio)tetrathiafulvalene]

disodium 4,5-dimercapto-1,3-dithiole-2-thione

ethanol (64-17-5)

sulfuric acid (7664-93-9)

methanol (67-56-1)

ether (60-29-7)

carbon tetrachloride,

CCl_4 (56-23-5)

nitrogen (7727-37-9)

mercuric acetate (1600-27-7)

acetone (67-64-1)

chlorobenzene (108-90-7)

potassium hydroxide (1310-58-3)

toluene (108-88-3)

2-propanol (67-63-0)

carbon disulfide (75-15-0)

1,2-dibromoethane (106-93-4)

chloroacetyl chloride (79-04-9)

N-chlorosuccinimide (128-09-6)

Triethylamine hydrochloride (554-68-7)

dichloromethane (75-09-2)

Succinimide (123-56-8)

magnesium sulfate,
 MgSO_4 (7487-88-9)

N-bromosuccinimide (128-08-5)

potassium xanthate

triethylamine (121-44-8)

Triethyl phosphite (122-52-1)

1,2-ethanedithiol (540-63-6)

trimethyl phosphite (121-45-9)

2-Oxo-1,4-dithiane (74637-14-2)

3-Chloro-2-oxo-1,4-dithiane (88682-21-7)

potassium O-(2-propyl) dithiocarbonate (140-92-1)

1,3-Dithiolo[4,5-b][1,4]dithiin, 2-(5,6-dihydro-1,3-dithiolo- [4,5-b][1,4]dithiin-2-ylidene)-5,6-dihydro-
(66946-48-3)

1,3,4,6-tetrathiapentalen-2,6-dione

2-Oxo-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin (74962-29-1)

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