



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

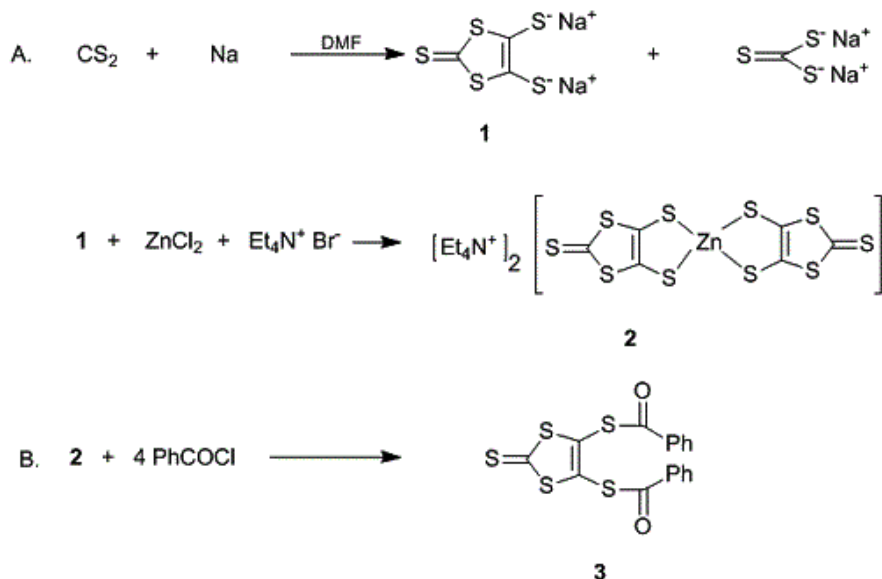
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions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

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## 4,5-DIBENZOYL-1,3-DITHIOLE-1-THIONE

[Benzenecarbothioic acid, S,S'-(2-thioxo-1,3-dithiole-4,5-diyl) ester]



Submitted by Thomas K. Hansen<sup>1</sup>, Jan Becher<sup>1</sup>, Tine Jørgensen<sup>1</sup>, K. Sukumar Varma<sup>2</sup>, Rajesh Khedekar<sup>3</sup>, and Michael P. Cava<sup>3</sup>.

Checked by John Hynes and Amos B. Smith, III.

### 1. Procedure

*CAUTION! The preparation should be carried out in an efficient hood, since carbon disulfide is both toxic and easily ignited.*

A. *Tetraethylammonium bis(1,3-dithiole-2-thione-4,5-dithiol) zincate (2)*. An oven-dried (105°C for 6 hr) apparatus consisting of a 3-L, round-bottomed flask, equipped with a mechanical stirrer (Note 1), a 250-mL pressure-equalizing dropping funnel, and a gas inlet tube, is connected to nitrogen (N<sub>2</sub>) via a Firestone valve (Note 2). To avoid water condensing on the surfaces, N<sub>2</sub> should be allowed to flow through the flask and out of the dropping funnel while the glassware is still hot. While the dropping funnel is temporarily removed, the flask is charged with 23.0 g of sodium shavings (1.0 mol) (Note 3) via a solids addition funnel (Note 4) and (Note 5) and, after reassembly, the apparatus is flushed with N<sub>2</sub> for 5 min and placed in an ice-water bath. Carbon disulfide (CS<sub>2</sub>, 180 mL, 3.0 mol) (Note 6) is introduced into the flask through the dropping funnel, after which the dropping funnel is immediately loaded with 200 mL of dimethylformamide (DMF) (Note 7), the system is closed, and the N<sub>2</sub> atmosphere is maintained throughout the reaction by adjusting the Firestone valve to a slightly positive pressure (Note 8). The DMF is added dropwise with stirring over 4 hr during which a red color appears (after addition of several mL of DMF). During the addition, the temperature of the reaction mixture is maintained with ice-water cooling. Upon completion of the addition, the reaction mixture is allowed to warm to room temperature and stir overnight, during which time it becomes increasingly deep red/violet. The reaction mixture is visually inspected for residual sodium (Note 9). As a precaution, ice is added to the cooling bath and 50 mL of methanol is added slowly through the dropping funnel (Note 9). A mixture of 400 mL methanol and 500 mL of deionized water, which is degassed by applying vacuum, is then added rapidly through the dropping funnel. A solution of 20 g (0.15 mol) of zinc chloride (ZnCl<sub>2</sub>) in a mixture of 500 mL of concentrated aqueous ammonium hydroxide and 500 mL of

methanol is then added through the dropping funnel (Note 10). A solution of 53 g (0.25 mol) of tetraethylammonium bromide in 250 mL of deionized water is added dropwise via the dropping funnel with vigorous stirring over at least 4 hr, and the solution is stirred overnight. A large amount of red precipitate develops in the flask overnight. This salt is collected by suction on a Büchner funnel and washed immediately with 500 mL of deionized water, then with 400-mL portions of isopropyl alcohol until the filtrate is colorless, and finally once with 200 mL of diethyl ether. The product is then dried in a desiccator under vacuum affording 74–76 g (83–84%) of zincate **2** as a red powder. The product is sufficiently pure for further reactions including alkylation and acylation (Note 11) and (Note 12).

B. *4,5-Dibenzoylthio-1,3-dithiole-1-thione* (**3**). A 1-L, round-bottomed flask, equipped for magnetic stirring, is charged with 400 mL of acetone (Note 13) and 16 g (0.0223 mol) of tetraethylammonium bis (1,3-dithiole-2-thione-4,5-dithio) zincate (**2**). Magnetic stirring is initiated, 40 mL (48.4 g, 0.345 mol) of benzoyl chloride (Note 14) is added via a dropping funnel over 4 hr, and the mixture is left overnight. The resulting yellow-light brown precipitate is collected by suction and washed on the filter with 500 mL of deionized water and 300 mL of acetone. This crude material is dissolved in 350 mL of chloroform, 0.5 g of Norit is added and the mixture heated under reflux for 10 min (Note 15). The mixture is filtered while still hot, and the filter cake washed with an additional 50 mL of hot chloroform to dissolve any residual product on the filter. The combined chloroform solutions are concentrated to 150 mL by use of a rotary evaporator. The resulting mixture is warmed to effect complete solution of diester **3** and 50 mL of methanol is added portionwise with stirring. The solution is then left overnight in the refrigerator. The resulting crystalline precipitate is collected by suction and air-dried, affording 11.8–12.0 g (65–66%) of dibenzoyl ester **3** (mp 143–144°C) (Note 16)

## 2. Notes

1. The mechanical stirrer must be made of inert material (glass or Teflon).
2. If a Firestone valve (Ace Glass Inc., Vineland NJ) is not available, a bubbler connected to the N<sub>2</sub> inlet tube via a T-adaptor is sufficient.
3. Sodium shavings (23.0 g, 1 mol) are conveniently prepared in the following way: A clean piece of sodium, 40–60 g, is weighed. Shavings are prepared from this using a commercial household grater directly into a beaker containing dry ether. The weight of shavings is determined by differential weighing of the remaining piece of sodium. *CAUTION: Sodium is a corrosive and potentially flammable solid. Handle with care using appropriate gloves for protection in a hood avoiding contact with moisture.*
4. *Extreme caution is necessary during the preparation and transfer of the sodium shavings because of the large amount of sodium placed in the flask.* The flask must be free of flaws and sodium waste must be carefully destroyed with ethanol.
5. Decanting the ether off immediately before addition is recommended to avoid oxidation of the shavings. If the shavings are a little wet from ether this does not harm the reaction.
6. The CS<sub>2</sub> was HPLC grade obtained from Aldrich Chemical Company, Inc. and used without purification. Lower grades of CS<sub>2</sub> can be used; however, a minor decrease in yield will occur.
7. The DMF used was obtained from Fisher Scientific Company (certified A.C.S.) and used without further purification.
8. It is important that the stirrer assembly be nearly gas tight, so that only small amounts of N<sub>2</sub> and CS<sub>2</sub> are lost.
9. Normally there will not be any sodium metal left, but small pieces of sodium may have adhered to the walls of the flask above the liquid level. These pieces of residual sodium metal must be destroyed with methanol. If any sodium is left, gas evolution is seen and the mixture is left for 1 hr with cooling and stirring.
10. This is most easily accomplished by adding the ZnCl<sub>2</sub> in portions to the rapidly stirred ammonium hydroxide followed by addition of the methanol.
11. Recrystallization of the zinc complex can be carried out as follows: Dissolve 20 g of the salt in 300 mL of warm acetone and add 0.5 g of Norit. Heat at reflux for 10 min, filter the hot mixture to remove the Norit, concentrate the filtrate under reduced pressure to one half the original volume, and add 100 mL of isopropyl alcohol. Collect the resulting precipitate by suction and wash the precipitate with ether. Provides 15.8 g (~80% recovery) of pure salt (mp 206–208°C).
12. The product exhibits the following properties: IR (KBr) cm<sup>-1</sup>: 1460, 1410, 1165, 1050, 986, 878,

775, 450;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.9, 53.2, 136.3, 209.5.  
13. Commercial acetone was first dried with  $\text{CaCl}_2$ , then distilled.  
14. Benzoyl chloride was obtained from Merck & Company, Inc., and used without purification.  
15. Any brand of decolorizing charcoal may be used.  
16. The product exhibits the following properties: IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3001, 1695, 1601, 1586, 1450, 1200, 1179, 1068, 880, 660, 637;  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ )  $\delta$ : 127.8, 129.0, 133.5, 134.6, 134.8, 185.2, 212.1.

### 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

This synthesis provides easy and inexpensive access to the 4,5-dithio-1,3-dithiole-2-thione system. By alkylation with 1,2-dibromoethane, 4,5-ethylenedithio-1,3-dithiole-2-thione, a key intermediate in the synthesis of bis(ethylenedithio)tetrathiofulvalene (BEDT-TTF) is obtained.<sup>4,5</sup> BEDT-TTF forms charge-transfer salts, many of which are conducting and superconducting, and known as "organic metals". Extensive reviews on the synthesis and properties of BEDT-TTF<sup>6</sup> and other TTF derivatives have been published.<sup>7</sup>

Originally, the reduction of carbon disulfide was carried out electrochemically, but this procedure is not practical for preparative amounts of material.<sup>8</sup> In 1979, a chemical reduction method was discovered by Steimecke.<sup>9</sup> The present procedure is based on that 1979 report, but sodium is substituted for potassium (which presents an explosive hazard).<sup>10</sup> Practical improvements have allowed the development of a one-pot procedure that is easily scaled up to provide 70–80 g of material.

Complexation with zinc effectively separates the  $\text{C}_3\text{S}_5$  dianion from the trithiocarbonate ion in high yield, and the material obtained is sufficiently pure for further reactions. The quaternary ammonium zincate salt is alkylated slowly but smoothly by many halides at room temperature in solvents such as acetone or tetrahydrofuran. Reaction of the zincate with benzoyl chloride followed by cleavage of the resulting benzoate by sodium ethoxide in ethanol provides the much more reactive species  $\text{Na}_2\text{C}_3\text{S}_5$ . The sodium salt is, however, very air sensitive,<sup>5</sup> whereas the zinc salt is completely stable.

An alternative to this synthesis is provided by Shumaker via tetrathiapentalene.<sup>11</sup> For most purposes, this procedure offers no advantages and requires more expensive starting materials. The procedure described here is applicable not only for the preparation of BEDT-TTF, but intermediates **2** and **3** may also be used for the synthesis of a variety of BEDT-TTF analogs.<sup>12 13</sup>

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### References and Notes

1. Department of Chemistry, Odense University, Campusvej 55, DK-5230, Odense M., Denmark.
2. Pilkington Technology Centre, Hall Lane Latham Ormskirk, L40 5UF Lancashire, England.
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

Tetraethylammonium bis(1,3-dithiole-2-thione-4,5-dithiol) zincate

BEDT-TTF

tetraethylammonium bis(1,3-dithiole-2-thione-4,5-dithio) zincate

[ethanol](#) (64-17-5)

[methanol](#) (67-56-1)

[ether,](#)  
[diethyl ether](#) (60-29-7)

[chloroform](#) (67-66-3)

[nitrogen](#) (7727-37-9)

[acetone](#) (67-64-1)

[Norit](#) (7782-42-5)

[benzoyl chloride](#) (98-88-4)

[zinc](#) (7440-66-6)

[sodium](#) (13966-32-0)

[isopropyl alcohol](#) (67-63-0)

[sodium ethoxide](#) (141-52-6)

[carbon disulfide](#) (75-15-0)

[1,2-dibromoethane](#) (106-93-4)

[zinc chloride](#) (7646-85-7)

[ammonium hydroxide](#) (1336-21-6)

[potassium](#) (7440-09-7)

[Tetrahydrofuran](#) (109-99-9)

dimethylformamide,  
DMF (68-12-2)

tetraethylammonium bromide (71-91-0)

4,5-Dibenzoyl-1,3-dithiole-1-thione

4,5-ethylenedithio-1,3-dithiole-2-thione

bis(ethylenedithio)tetrathiofulvalene

4,5-Dibenzoylthio-1,3-dithiole-1-thione

Benzenecarbothioic acid, S,S'-(2-thioxo-1,3-dithiole-4,5-diyl) ester (68494-08-6)