Pergamon

Tetrahedron Letters 43 (2002) 1553–1554

TETRAHEDRON
LETTERS

A convenient and improved synthesis of dithieno[3,2-*b*:2′,3′-*d*]thiophene

Fredrik Allared, Jonas Hellberg* and Tommi Remonen†

Department of Organic Chemistry, Royal Institute of Technology, Teknikringen 56, S-100 44 Stockholm, Sweden

Received 4 December 2001; accepted 21 December 2001

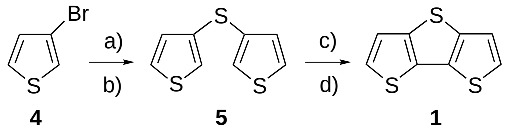
Abstract—An improved synthesis of dithieno[3,2-*b*:2′,3′-*d*]thiophene **1** is presented. By starting from 2,3-dibromothiophene **2** the total yield was improved from 35 to 58%. We also describe a more convenient synthesis of one of the reagents, benzenesulfonic acid thioanhydride **3**. © 2002 Elsevier Science Ltd. All rights reserved.

Dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) **1** has found use in materials for electronic and optical applications. Optical phenomena such as two-photon absorption,[1,2] electro-luminescence,[3,4] photochromism,[5] and two-photon excited fluorescence[6] in DTT-based materials have been investigated. The DTT-system has attracted interest as a building block for dimeric systems that can be used as the active component in thin film transistors.[7–9] These transistors have shown interesting device characteristics, e.g. high mobilities and large on/off ratios. Organic acceptor and donor molecules based on DTT have been synthesized and used for the preparation of different cation radical salts and charge-transfer complexes.[10–14] Conducting polymers based on DTT have also been made.[15,16]

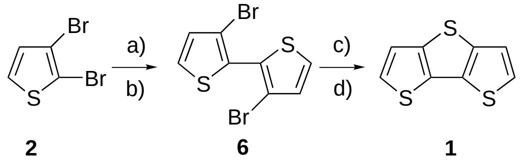
One of the factors hampering further exploration of the dithienothiophene family is the inefficiency of the presently used synthesis.[17]

The old synthesis is depicted in Scheme 1. 3-Bromothiophene **4** is lithiated with *n*-butyllithium and reacted with benzenesulfonic acid thioanhydride **3**. The resulting 3,3′-dithienylsulfide **5** is again treated with *n*-butyllithium and then with cupric chloride, to yield the desired target **1**. In our hands the total yield has varied from 10% up to 35% (which is the reported yield). These low yields can be attributed mainly to the low-yielding distillation of the dithienyl sulfide **5**, and to an anticipated low selectivity of the lithiation of **5** in the second step.

Our improved synthesis of **1** is depicted in Scheme 2. Lithiation of 2,3-dibromothiophene **2** using *n*-butyllithium followed by oxidative coupling with cupric chloride according to the literature procedure[18,19] gave, after recrystallization from hexanes, 79% of the desired 3,3′-dibromo 2,2′-bithiophene **6**. In the second step, **6** was dissolved in diethyl ether (10 ml/mmol), and cooled to −78°C under nitrogen. After addition of 2 equiv. of *n*-butyllithium and 40 min of stirring, 1 equiv. of **3** was added, and the mixture was left to reach room temperature overnight. Normal work-up and purification by



Scheme 1. Usual route to dithieno[3,2-*b*:2′,3′-*d*]thiophene **1**. *Reagents and conditions*: (a) *n*-BuLi, −78°C; (b) $(PhSO_2)_2S$ **3**, −78°C to rt; (c) *n*-BuLi, −78°C; (d) $CuCl_2$, −78°C to rt.



Scheme 2. New synthesis of dithieno[3,2-*b*:2′,3′-*d*]thiophene **1**. *Reagents and conditions*: (a) *n*-BuLi, −78°C; (b) $CuCl_2$, −78°C to rt (79%); (c) *n*-BuLi, −78°C; (d) $(PhSO_2)_2S$ **3**, −78°C to rt (70%).

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* Corresponding author. Tel.: +46-8-7908127; fax: +46-8-7912333; e-mail: jhel@kth.se

† Present address: Acreo AB, Bredgatan 34, S-602 21 Norrköping, Sweden.

PII: S0040-4039(02)00006-0

chromatography or recrystallization from methanol gave 70% yield of pure dithieno[3,2-*b*:2′,3′-*d*]thiophene. We found that it was necessary to grind the benzenesulfonic acid thioanhydride **3** finely; when large crystals of **3** were used, macrocyclic by-products were formed. We had earlier observed, but not fully understood, this problem in the synthesis of the tetramethylsubstituted dithieno[3,2-*b*:2′,3′-*d*]thiophene.[20] 3,3′-Dibromo 2,2′-bithiophene **6** can also be obtained by tetrabromination–debromination of 2,2′-bithiophene.[21] This procedure can be readily scaled up.

To further improve the synthesis and make it more convenient, we looked at the synthesis of the benzenesulfonic acid thioanhydride **3** used in the last step. Although the published synthesis gave decent yields of **3**, the product showed varying shelf life. We tried to replace benzene with toluene, but the higher boiling point of toluene accelerated degradation of **3** during recrystallization. Instead we found diethyl ether to be a suitable solvent. The benzenesulfinic acid sodium salt dihydrate was slurried in ether and 0.5 equiv. of sulfur dichloride (twice distilled from phosphorus trichloride) was added over 15 min. After 2 h the reaction was stopped by the addition of water and the insoluble product was filtered off and rinsed with water. Recrystallization from acetone gave an 80–90% yield of **3** as large white crystals with excellent stability in ambient atmosphere and temperature.

The main advantages of this improved synthesis are: (a) the crystallinity of the bithiophene **6**, (b) the regioselective lithiation of the two brominated positions in **6**, and (c) the improved quality of **3**. All these factors improve the yield and purity of the product.

Acknowledgements

Financial support from the Royal Institute of Technology, Swedish Natural Science Research Council and the Ernst Johnson foundation is gratefully acknowledged.

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