ORGANIC LETTERS

2004
Vol. 6, No. 20
3437−3439

A New Route to Annulated Oligothiophenes

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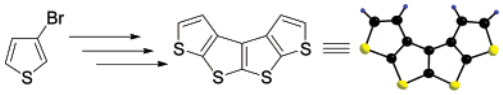
Received June 18, 2004

ABSTRACT

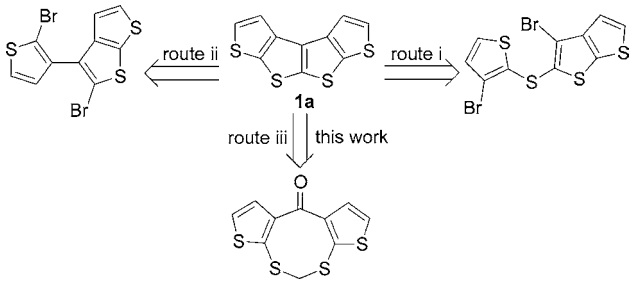


A new convenient method for the construction of thiophene-annulated thieno[2,3-*b*]thiophenes has been proposed. The key step of the method is ring closure of 10*H*-bisthienodithiocin-10-one by strong bases. The syntheses of two previously unknown annulated oligothiophenes, thieno-[2,3-*b*]thieno[3′,2′:4,5]thieno[3,2-*d*]thiophene (1a) and thieno[3,2-*b*]thieno[2′,3′:4,5]thieno[3,2-*d*]thiophene (1b), have been described to illustrate the success of the method.

Annulated oligothiophenes (AO) have been known for about 50 years.[1] In the past few years, there has been a resurgence of interest in synthesis of AO.[2−4] AO are important building blocks for a wide variety of materials for electronic and optical applications such as electroluminescence,[5] two-photon absorption,[6] excited fluorescence,[6] photochromism,[7] and nonlinear optical chromophores.[8] Some AO systems, which have been employed in thin-film transistors, have shown high mobilities and on/off ratios.[9] Organic acceptor and donor molecules based on AO have been synthesized and used for the preparation of different cation radical salts and charge-transfer complexes.[10] Conducting polymers based on AO have also been made.[11]

All isomeric thienothiophenes and dithienothiophenes and several compounds containing more than three condensed thiophene rings are known to date. Existing synthetic approaches to dithienothiophenes and higher annulated oligothiophenes are based on route i or ii (Scheme 1).[12−14]

Scheme 1. Retrosynthetic Approaches toward Trithienothiophenes



Unfortunately, these methods have a drawback, because of the difficult access to some starting materials and low yields.

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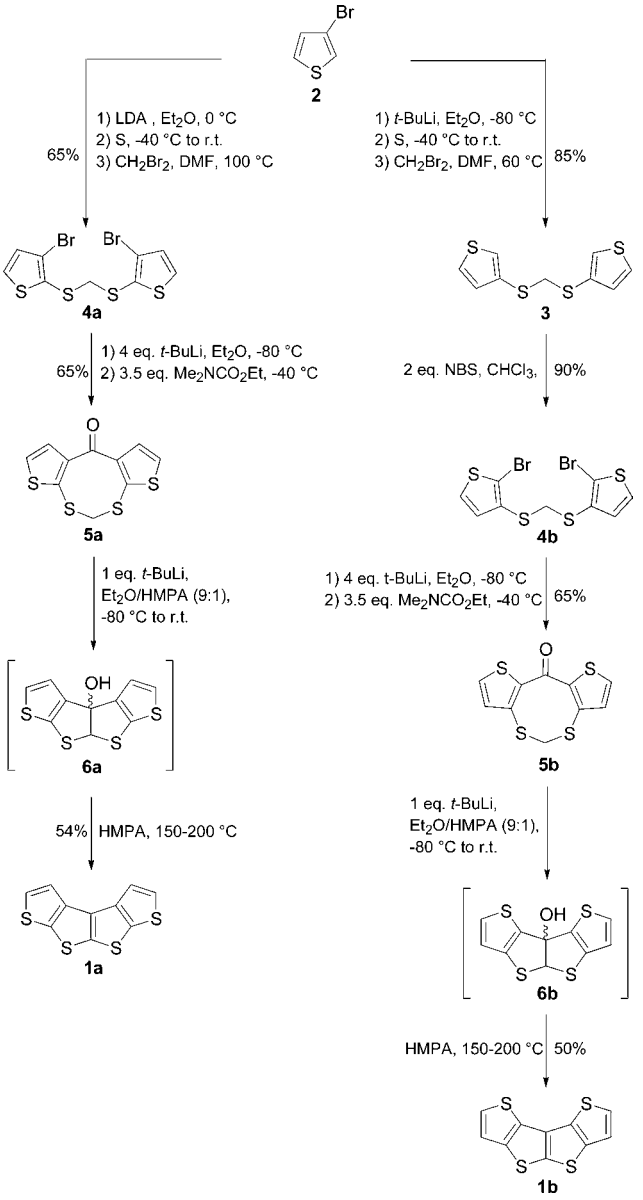
10.1021/ol048835s CCC: $27.50
Published on Web 08/31/2004

Hence, there is a necessity to develop novel synthetic approaches to higher annulated oligothiophenes.

Herein we describe short scalable syntheses of two previously unknown isomeric trithienothiophenes (**1a**, **1b**) in an illustration of a new general strategy for the preparation of annulated polyarylenes containing a thieno[2,3-*b*]thiophene moiety (Scheme 1, route iii). The key step of the method involves cyclization of 10*H*-bisthienodithiocin-10-one (**5a**, **5b**). Syntheses of **1a** and **1b** are proposed to start from cheap, commercially available starting material, 3-bromothiophene (**2**) (Scheme 2).

Scheme 2. Synthesis of Trithienothiophenes



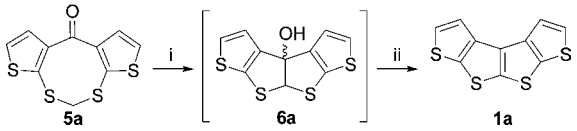
The intermediates for the synthesis of **5a** and **5b** are isomeric *bis*-dibromothienylsulfanyl-methanes (**4a**, **4b**). We elaborated a one-pot procedure for the preparation of **4a** from **2**.[15] The treatment of 3-bromothienyl-2-lithium with sulfur followed by the addition of 1 equiv of dibromomethane gave target **4a** in 65%. While using calculated 0.5 equiv of dibromomethane, we obtained **4a** in less than 35% yield.

Isomeric **4b** was prepared in two steps from **2** via **3**. 3-Thienyllithium was treated with 1 equiv of sulfur, and the resulting lithium thiolate was alkylated with 0.5 equiv of dibromomethane to give, after distillation in portions (no more than 0.05 mol), **3** in 85% yield. In the second stage, subsequent treatment of **3** with 2 equiv of NBS gave **4b** in 90% yield. Ketones **5a** and **5b** have been prepared from the lithium derivatives and *N*,*N*′-dimethylethylcarbamate, which is known as one of the best and very convenient reagents for the synthesis of symmetric aryl ketones.[16,17] Lithiation of **4a** and **4b** using 4 equiv of *t*-BuLi followed by addition of 3.5 equiv of *N*,*N*′-dimethylethylcarbamate gave **5a** and **5b** in 65% yield.

Target compounds **1a** and **1b** were obtained by the cyclization of **5a** and **5b** with strong bases followed by the dehydration of the formed alcohols.

Optimization of the reagents and reaction conditions for this stage is outlined in Table 1. The application of LDA in ether as a base and BF_3 etherate as a dehydrating agent gave trithienothiophene **1a** from **5a** in very low yields (Table 1, entries 1 and 2).[18,19] On the other hand, the addition of HMPA (10%) and heating in this solvent led to **1a** in 44% isolated yield.[20] The further optimization of the reaction conditions showed that *t*-BuLi and Et_2O/HMPA 9:1 are the reagents of choice, and the yield of **1a** was increased to 54% (entry 5).[21]

Table 1. Optimization of Final Steps



entry	step i	step ii	yield (%)
1	LDA, c = 0.1 mol/L, Et_2O	BF_3·Et_2O, r.t., 5 min	trace
2	LDA, c = 0.01 mol/L, Et_2O	BF_3·Et_2O, r.t., 5 min	5
3	LDA, c = 0.01 mol/L, Et_2O/HMPA (9:1)	150−200 °C, HMPA, 1 h	44
4	*t*-BuLi, c = 0.1 mol/L, Et_2O/HMPA (9:1)	150−200 °C, HMPA, 1 h	40
5	*t*-BuLi, c = 0.01 mol/L, Et_2O/HMPA (9:1)	150−200 °C, HMPA, 1 h	54

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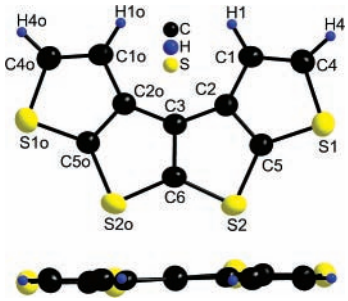

Figure 1. Crystallographic structure of compound **1a**.

Single crystals grown by slow crystallization **1a** from *o*-dichlorobenzene were analyzed by X-ray diffraction method. The obtained crystallographic structure definitely confirms the expected fully planar geometry of molecule **1a** (Figure 1). It is interesting that angle $C4C1-C4_OC1_O = 171°$ is close to 180°.

In summary, we proposed a novel synthetic strategy to annulated polyarylenes containing a thieno[2,3-*b*]thiophene moiety. We elaborated a simple straightforward procedure for the synthesis of **1a** and **1b** that is easily scalable and permits multigram preparations. We believe, that further development of this method will allow synthesis of other isomeric trithienothiophenes, as well as their benzo- and heterocyclic analogues.

Acknowledgment. Financial support from the Russian Foundation for Basic Research (Grant N 03-03-32024-a) is gratefully acknowledged.

Supporting Information Available: Experimental details, characterization data for all new compounds, and X-ray data for compound **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL048835S