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A new reaction of P_4S_{10} and Lawesson's reagent; a new method for the synthesis of dithieno[3,2-*b*;2′,3′-*d*]thiophenes

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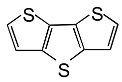
Abstract—A new reaction of P_4S_{10} and Lawesson's reagent for the synthesis of fused thiophenes has been uncovered. It has given easy access to the synthesis of derivatives of the technologically important heterocycle dithieno[3,2-*b*;2′,3′-*d*]thiophene, DTT. Electrochemical polymerization of one of the derivatives has been demonstrated.

Dithieno[3,2-*b*;2′,3′-*d*]thiophenes (DTT) **1** are important building blocks of a wide variety of materials for electronic and optical applications such as electroluminescence,[1,2] two-photon absorption,[3,4] excited fluorescence,[3] photochromism[5] and nonlinear optical chromophores.[6] Dimer DTT-systems, which have been employed in thin film transistors, have shown high mobilities and on/off ratios.[7–9] Conducting polymers[10–12] and organic acceptor and donor molecules for the preparation of different cationic radical salts and charge-transfer complexes[13–16] have been prepared. Recently, DTT dioxides having high photoluminescence efficiency[17] have also been synthesized.

Unfortunately, the limited availability of synthetic methodologies for the synthesis of such an important heterocyclic material bearing various functional groups has been hampering its further exploration. The currently used synthetic method, which requires lithiation and coupling using $CuCl_2$, gives low yields possibly due to the poor selectivity of the lithiation reaction and an inefficient work-up such as a low yielding distillation.[18] Although, recently, this method has been claimed to have been improved[19] and an alternative synthetic methodology has been reported,[20] it is still important to make synthetic contributions, particularly for the synthesis of dithieno[3,2-*b*;2′,3′-*d*]thiophenes with versatile functional groups, which will enable an in depth exploration.



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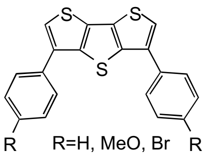

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Here we report a new and concise synthesis of a DTT **2** having functional groups at the 3- and 5-positions, which are available for further functionalization. This method opens up a way to form dithienothiophenes via a one-pot two ring-closure reaction of α-dithioketones at the 3- and 4-positions of the thiophene ring (Scheme 1). The synthesis of the target molecule required four steps starting with tetrabromination of thiophene **3** with Br_2, which gave 95% of tetrabromothiophene **4**. Selective removal of the bromines at the 2- and 5-positions was carried out using Zn to yield 85% of 3,4-dibromothiophene **5**, to which α-thioketones at the 3- and 4-positions were introduced via a one-pot, three step reaction; (i) lithiation with *n*-BuLi at −78 °C, (ii) addition of sulfur and (iii) introduction of α-thioketones by adding α-bromoketones to the mixture. The yields varied from 50% to 58%, depending on the nature of the R group (55%, R = H; 50%, R = Br; 58%, R = MeO). The crucial dual ring closure was achieved by treatment of the diketone **6** with P_4S_{10} in boiling anhydrous toluene, which took nearly 3 h to complete. Yields of 43%, 45%

Keywords: Phosphorus pentasulfide; Lawesson's reagent, (LR); Dithienothiophene, DTT.

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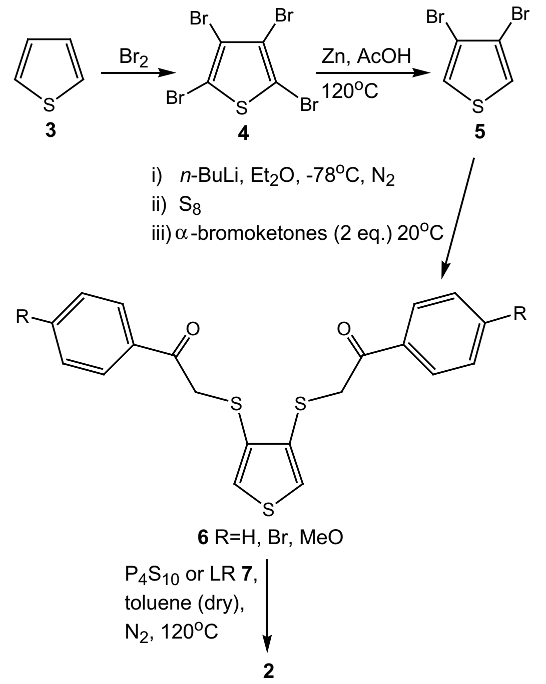
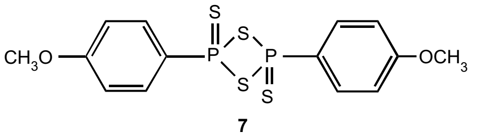


Scheme 1.

and 50% were obtained for the compounds with R groups H, Br and MeO, respectively, and the overall yield for the four steps varied from 19% to 24%.[21] When the reaction was repeated, this time using Lawesson's reagent (LR) **7**, which required overnight reflux to complete, lower yields were obtained, 15%, 18% and 22% for the compounds with R groups H, Br and MeO, respectively.

In order to understand the driving force of the ring-closing reactions, the diketone, **6** was refluxed in toluene with HCl and in neat toluene overnight. In both cases only the starting material was recovered. These results indicated that the presence of P_4S_{10} or LR during the ring-closing reaction was essential.



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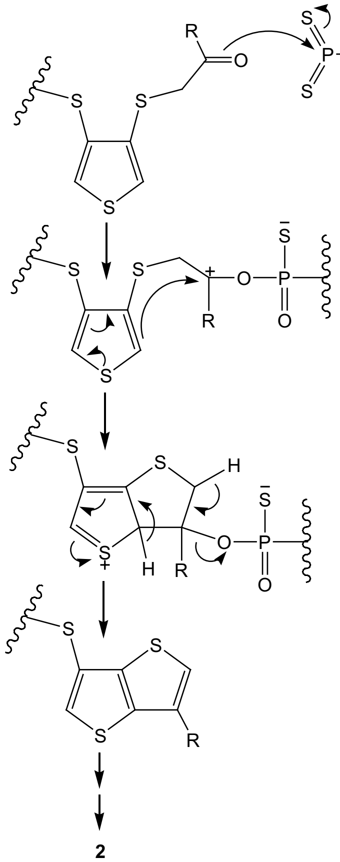
It is well known that P_4S_{10} and LR are used to convert ketones to thiones,[22–24] which may suggest that the initial step for the in situ two ring-closing reactions could be the production of dithiones. Clearly, this cannot take place here. Instead, possibly, the initial attack by the ketone to the phosphothione, which is a decomposition product of LR or P_4S_{10}, is followed by attack from C-2 of the thiophene, which leads to the formation of the first thiophene ring. The same mechanism involving the other ketone and a similar attack, this time from C-5, leads to the formation of the second thiophene ring, which results in the production of the disubstituted dithieno[3,2-*b*;2′,3′-*d*]thiophene heterocycle (Scheme 2).



Scheme 2.

Polymerization of DTT **2** (R = H) was performed electrochemically using Pt working, Pt counter and Ag/Ag$^+$ reference electrodes in 0.1 M $NaClO_4$–MeCN solution (Fig. 1). Deposition of the polymer on the electrode surface was observed as a function of the rise of oxidation current at 1.33 mV and the rise of oxidation/reduction peaks. Reduction took place at 1.06 mV. The

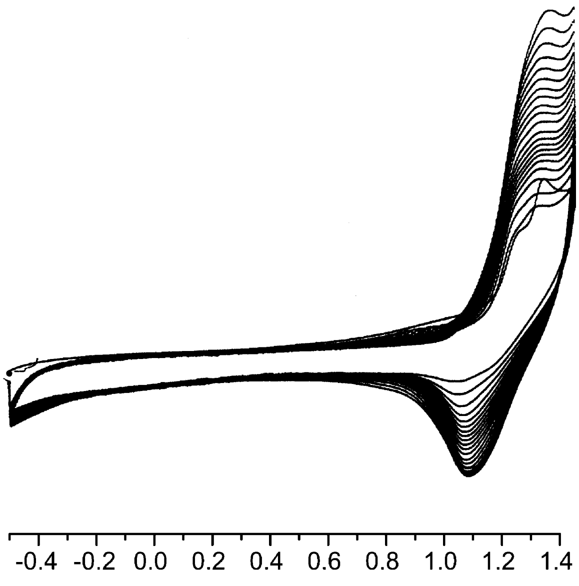


Figure 1. Polymerization of DTT **2** (R = Ph). MeCN, $NaClO_4$ (0.1 M) versus Ag/AgCl, 100 V s^{-1}, 1.1×10^{-3} M.

polymer film was then washed with MeCN and placed in a monomer free solution (0.1 M $NaClO_4$–AcCN), CV analysis of which showed a linear increase of both oxidation and reduction peaks, which indicates an electrode supported electroactive film.

In conclusion, we disclose a new and concise reaction of P_4S_{10} and LR with ketones, which provides easy access to the synthesis of derivatives of the technologically important material DTT. In connection with this study, the investigation of the properties of compounds **2** and the synthesis of new derivatives and their polymers are in progress.

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21. Compound **2** R = H: mp 130–132 °C; Anal. Calcd for $C_{20}H_{12}S_3$: C 68.96, H 3.44 found: C 68.99, H 3.38; FABMS m/e 348 (M^+); ^1H NMR (200 MHz, $CDCl_3$) δ 7.81 (d, $J = 7.4$ Hz, 4H, Ph), 7.42 (m, 8H, Ph+thiophene); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 135.9, 134.5, 131.3, 129.0, 128.4, 127.5, 126.6, 121.3.
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