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Simple one-step synthesis of 3,4-dimethoxythiophene and its conversion into 3,4-ethylenedioxythiophene (EDOT)

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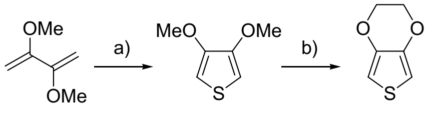
Abstract—3,4-Dimethoxythiophene (**2**) was synthesized in one-step from readily available bulk chemicals via a ring closure reaction, and was then *trans*-etherified with ethylene glycol to give 3,4-ethylenedioxythiophene (**3**) (EDOT).

Poly and oligothiophenes are of paramount importance in the field of organic electroactive materials.[1] Many of the most promising polymers and oligomers for such applications are derivatives of EDOT (**3**).[2] For instance, poly(3,4-ethylenedioxythiophene) (PEDOT) is produced on a yearly several-ton scale and is commercially available as a random copolymer with poly(*p*-styrene-sulfonate).[3] Despite its high price,[4] this blend is often used in several different electronic applications.[5] Monomer **3**, from which PEDOT is synthesized, is traditionally prepared according to a five-step reaction scheme[6] that suffers from several major drawbacks from an industrial point of view, including dependence on strong bases, carcinogenic reagents (such as 1,2-dibromoethane), high temperatures, pressure build-up and potential run-away reactions. Conventionally, compound **2** is also prepared in the same lengthy manner[7,8] (Scheme 1).

We herein wish to report on a novel and advantageous method to prepare 3,4-dimethoxythiophene (**2**)—a valuable precursor in thiophene chemistry—via a simple one-step reaction from cheap and common bulk chemicals. We also show that thiophene **2** can be *trans*-etherified with ethylene glycol to give the precious monomer EDOT (**3**), in a single second step.



1 **2** **3**

Scheme 1. Reagents and conditions: (a) NaOAc, SCl_2 in hexanes, 5 °C to rt; (b) ethylene glycol, cat. *p*-TsOH in refluxing toluene.

Our synthesis of **2** relies on a ring closure (addition–elimination) between 2,3-dimethoxy-1,3-butadiene (**1**) and sulfur dichloride in hexane together with an insoluble 'buffer'. To the best of our knowledge, only one comparable ring closure reaction to give a thiophene has been reported before.[9] In this case, the authors used dichloromethane as solvent, in which a 1,3-butadiene and sulfur dichloride were allowed to react at low temperature, followed by evaporation and addition of potassium *t*-butoxide in DMSO for the elimination of 2 equiv of hydrogen chloride to occur. This gave, after work-up, a thiophene in low yield (12–15%). We believe that many side reactions may be circumvented by changing to a nonpolar solvent such as hexane, in which hydrogen chloride has a limited solubility, and by avoiding strong bases. Moreover, we employ sodium acetate as a buffer to protect the sensitive product from decomposition during formation and work-up.

2,3-Dimethoxy-1,3-butadiene (**1**) is readily available in multigram quantities from biacetyl and trimethyl orthoformate, according to a scaled-up literature procedure.[10] Sulfur dichloride of technical grade (appr. 80%) was purchased and distilled before use.[11] In a typical experiment, butadiene **1** was added to a cold slurry (5 °C) of dry sodium acetate (3 molar equiv) in hexanes (0.3 M). Sulfur dichloride in hexanes (50% v/v) was added over 30 min and the resulting mixture allowed to reach room temperature overnight. The

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buffer material was filtered off and the crude product purified by vacuum distillation, to give pure thiophene **2**. The yield was 60% on a 50 mmol scale. This reaction was also run several times on a 1 mol scale, using only standard laboratory equipment, and gave the desired product in slightly diminished yield. It should be emphasized that if the buffer material was omitted, only very little product could be collected (<5%). Additionally, no addition of base at the end of the reaction was necessary to ensure aromatization; the elimination of hydrogen chloride may very well be catalyzed by sodium acetate as well. As has been noted before, thiophene **2** is relatively unstable, especially when contaminated,[7] and should either be stored at low temperatures under inert atmosphere or be used immediately.

3,4-Dimethoxythiophene (**2**) has previously been *trans*-etherified with alcohols,[12] 1,2-diols,[13] monothiols and 1,2-dithiols[14] and 2-mercaptoethanol.[15] Much to our surprise, however, no reaction between **2** and plain ethylene glycol to give EDOT (**3**) prior to this report is to be found in the literature. In our hands, thiophene **2** was indeed straightforwardly converted into EDOT (**3**) with ethylene glycol under standard conditions (catalytic amounts of *p*-toluenesulfonic acid in refluxing toluene). The crude product was purified by column chromatography or vacuum distillation and gave pure EDOT (**3**) in good yield (65%).

In conclusion, we have shown that the valuable precursor 3,4-dimethoxythiophene (**2**) may be synthesized in one simple step on a multigram scale from cheap bulk chemicals. We have also confirmed that **2** is easily *trans*-etherified with ethylene glycol to give EDOT (**3**), a key monomer in the field of organic electroactive materials, in good overall yields. Our method should be well suited for industrial scale production.

Acknowledgements

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