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Efficient synthesis of 2,5-dicarbonyl derivatives of 3,4-ethylenedithiothiophene (EDTT) via addition-elimination reaction

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ABSTRACT

Derivatives of 3,4-ethylenedithiothiophene (EDTT) are reported starting from tetrabromothiophene. Selective 2,5-dilithiation followed by reaction with a range of aldehydes gives diols as mixtures of diastereomers. Only the 2 and 5 positions in thiophene react leaving the 3,4-bromides for further elaboration. The diols are oxidised to their corresponding diketones using activated MnO_2. Reaction with 1,2-ethanedithiol, by addition-elimination, provides access to novel monomers for the preparation of conjugated copolymers of 3,4-ethylenedithiothiophene (EDTT). A range of these monomers can be attained by applying the synthesis of a series of ketones applicable to further synthesis of π-extended thiophene-based organic semiconductors. Finally, this new route was compared to 3,4-ethylenedioxythiophene (EDOT) dialdehyde derivatives synthesised by an alternative to literature chemistry.

1. Introduction

From their initial mainstream uptake in the early 1980s oligothiophenes have risen to become one of the most privileged structures in the organic semi-conducting materials area.[1,2] By appropriate choice of thiophene substituents and microstructure (e.g. degree of oligomerisation, connectivity, use of additives, etc.) the resultant materials' (opto)electrical properties can be modulated with a high degree of precision. This ability to tune thiophene-based materials for a specific application has led to their widespread use in organic photovoltaics (OPV),[3] organic field effect transistors (OFET),[4] sensors[5] and particularly in electrochromic/electroluminescent (OLED)[6] applications. Such 'modular-materials' approaches have created an insatiable appetite for new thiophene sub-units from materials chemists for their inclusion into oligo(poly)thiophene structures as evidenced by the thousands of papers that have appeared in this area in the last 10 years. In particular, derivatives of 3,4-ethylenedioxythiophene (EDOT) **1** have proved popular targets as this monomer is easily polymerised to PEDOT-based polymers **3**[7] whose formulation with polymer supported sulfonates (PEDOT-PSS) now forms the backbone of many transparent electrode technologies. Recently, new thermoelectric (TE) applications for PEDOT-based materials have emerged,[8] potentially allowing direct conversion of waste heat into electrical power. For optimal TE devices the use of bulk, rather than thin film, configurations would be preferred (to maximise power-from-heat recovery). Although the low band gap of PEDOT-PSS (1.6 eV) favours high electrical conductivity[9] (vital for TE applications) the physical properties of current PEDOT-PSS co-polymers (solubility, mp) are less favourable for fabrication of bulk (mm) rather than thin film (~100 nm) devices. We considered the possibility that derivatives of the sulfur analogue of EDOT, that is EDTT **2**, might prove of utility in seeking more processible entities. Both EDTT itself and PEDTT are known versatile components in organic materials chemistry.[10] Although the band gap of PEDTT **4** is greater (2.2 eV) than PEDOT, building in functionality to allow the creation of vinyligous linkages at the 2,5-postitions of EDTT **2** should allow band gap reduction, as similar synergies have been noted in related structures.[11] The positioning of suitable groups to promote solubility and processability of bulk samples is also desirable.

Consequently, two main points are investigated in this paper. Firstly, the synthesis of new polymer precursors based on EDTT **2** that might have lower band gap potentials (essential for organic materials applications) even if these are based on PEDTT-like structures. Secondly, the potential structure of the new polymers should allow for the improved solubility characteristics required for

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many applications. Two general strategies are employed here in to target monomers for new polymers having small HOMO–LUMO energy differences and good solubility in the different solvents. The first involves increasing the conjugation of polymers by inserting an alkenyl unit (C=C) into the structure of the polymers, to attain a lower band gap. The second strategy involves strategic placement of alkyl groups whereby the side chain will increase the polymer solubility and thus improve its processability (see Scheme 1).

2. Results and discussion

2.1. Synthetic routes to derivatives of EDTT

Our initial study focused on methods to quickly and reliably attain 2,5-derivatives of 3,4-ethylenedithiothiophene (EDTT) **2** starting from the readily available crystalline tetrabromothiophene **5** (Scheme 2).

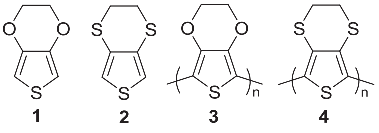
Tetrabromothiophene **5** is easily prepared on large scales by bromination of thiophene in 73% yield, the HBr by-product is conveniently quenched by collecting the off-gas into a suitable water trap. The activated 2,5 positions of **5** are cleanly exchanged with *n*BuLi at −78 °C. While rearrangements (the so called “halogen dance”[12]) can take place at higher temperatures, reactive electrophiles are expected to intercept the dilithiated intermediate cleanly. Relatively few investigations have employed this strategy but examples with: chlorotrimethylsilane,[13] a limited number of aldehydes[14] and acyl chlorides[15] are known. However, the reported yields can be poor in such procedures.

From a practical perspective, addition of the aldehyde at −78 °C followed by warming to −20 °C affords the maximum yield of **6a-e** (40–82%) by minimising organolithium rearrangement. Compounds **6a-e** are attained as a diastereomeric mixture but the *syn* and *anti* diastereomers could be separated by careful column chromatography. Each of the diastereomeric compounds 6**a-e** could be converted into the corresponding ketones **7a-e** using activated MnO_2, in refluxing dichloromethane. Simple overnight reaction is required to attain complete conversion. Ketones **8** are easily isolated by column chromatography as they appear as bright yellow bands. The resulting micro-crystalline yellow solids show spectra in accord with the proposed formulation. The presence of two keto functions allows potentially many condensation polymers to be accessed related, in part, to EDTT **2** and PEDTT **4**.

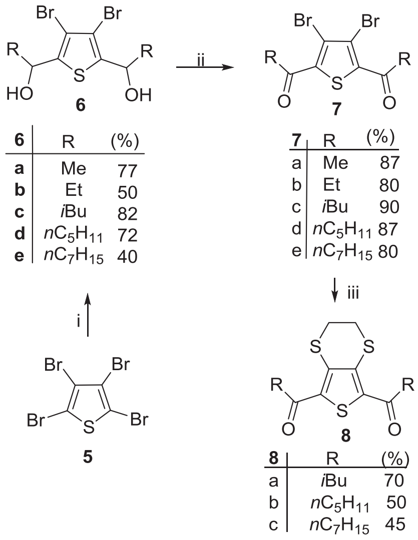
For comparison, the closest literature method for the synthesis of EDTT **2** we could identify is shown in Scheme 3.[16] This approach requires two steps from **9** to add the *bis*-thioether in 86% overall yield. In our approach (Scheme 2), compounds **8a-c** require only one step to install the same thioether. By the reaction of 1,2-ethanedithiol with compounds **7a-c** (in DMF and over 2 days in the presence of Na_2CO_3) more modest yields of 71, 50 and 45% are attained for **8a-c** respectively. For further comparison, the parent **2**, and its *S*,*O*-analogue, can be also prepared from **9** by the chemistry of Roncali.[17]

2.2. Synthetic routes to derivatives of EDOT

In the last few years 3,4-ethylenedioxythiophene (EDOT) **1** and its derivatives have become very important commercial compounds for the preparation of new organic materials.[7,18] However, most commercial routes to EDOT use $S(CH_2CO_2Me)_2$ and rely on late stage (wasteful) decarboxylation of the ester units. We wondered if a nitrile group was used instead if this could provide access to 2,5-disubstituted aldehydes closely related to our diketo-EDTT species **8**. This new route to derivatives of EDOT has been investigated as shown in Scheme 4.



Scheme 1. The structures of EDOT **1** and EDTT **2** and their derived polymers PEDOT **3** and PEDTT **4**.



6	R	(%)
a	Me	77
b	Et	50
c	*i*Bu	82
d	nC_5H_{11}	72
e	nC_7H_{15}	40

7	R	(%)
a	Me	87
b	Et	80
c	*i*Bu	90
d	nC_5H_{11}	87
e	nC_7H_{15}	80

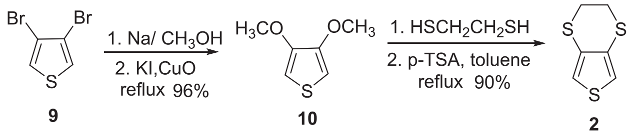
8	R	(%)
a	*i*Bu	70
b	nC_5H_{11}	50
c	nC_7H_{15}	45

Scheme 2. Synthetic route to ketothiophenes. Reagents and conditions: (i) THF/*n*BuLi, RCHO, −78 to −20 °C, 3 h; (ii), MnO_2 (10 equiv.), CH_2Cl_2, 40 °C, 16 h; (iii) 1,2-ethanedithiol (2.2 equiv.), DMF, Na_2CO_3, 16 h, r.t.

The intermediate **13** is prepared in two steps, the first uses the ultra-cheap starting material $Na_2S{\cdot}9H_2O$ for alkylation with chloroacetonitrile **11** in DME to yield compound **12** near quantitatively and in excellent purity which allows its use without purification. Subsequent reaction of **12** and diethyl oxalate prepares the potassium salt **13**, which is also used directly without further purification, to access the dinitrile **14** in modest yield. However, **14** is easily isolated analytically pure after a simple filtration through a silica plug. Finally, **14** was converted to the corresponding aldehyde **15** by its treatment with DIBAL-H at 0 °C in anhydrous toluene. Compound **15** is already recognised as an important intermediate in the synthesis of thiophene-based semiconductor polymers.[19,20]

3. Conclusions

We have successfully found a new route to homologs of 3,4-ethylenedithiothiophene (EDTT) **2** having ketone functionalities at the 2,5-positions. From tetrabromothiophene **5**, monomers **8a-c** were obtained in three steps. In addition, the monomers **8a-c** are attractive species for the future synthesis of many thiophene-based semiconductor polymers. Additionally, we have reported a new route for the synthesis of the 2,5-diformyl derivative of 3,4-ethylenedioxythiophene (EDOT), the key intermediate **14** is obtained using ultra-cheap $Na_2S{\cdot}9H_2O$ in just three steps. Finally,



Scheme 3. One comparitive route for EDTT **2**.[16]