

## General, Efficient Route to Thiophene-1-Oxides and Well-Defined, Mixed Thiophene-Thiophene-1-Oxide Oligomers

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Thiophene-1-oxides have attracted considerable attention due to their highly reactive nature, their biochemical roles in metabolism and toxicology,<sup>1</sup> and because the development of general methods for their preparation has proven difficult.<sup>2</sup> Chemically they behave as reactive dienes, which tend to decompose via Diels–Alder dimerization.<sup>2,3</sup> In a few cases, sterically protected thiophene-1-oxides have been prepared via oxidation of the corresponding thiophenes, but this route appears to be complicated by rapid, further oxidation to the 1,1-dioxides.<sup>2</sup> The reaction of tetraphenylzirconacyclopentadiene, Cp<sub>2</sub>ZrC<sub>4</sub>Ph<sub>4</sub>, with thionyl chloride has been shown to give tetraphenylthiophene-1-oxide (**2a**) in moderate yield,<sup>4</sup> but we have found that this method is not generally reliable for the synthesis of thiophene-1-oxides (vide infra).

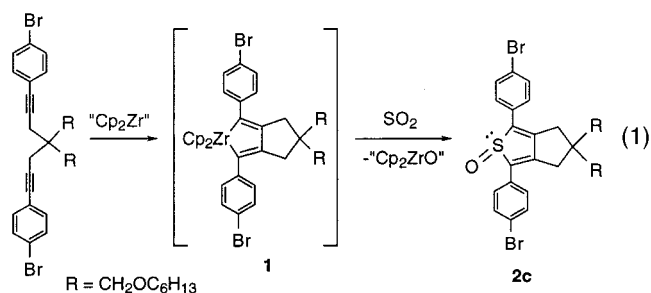
We have been exploring the use of zirconocene couplings in the synthesis of  $\pi$ -conjugated polymers and oligomers with novel electronic properties<sup>5</sup> and have recently targeted materials with high electron affinities that might display n-type semiconductor properties.<sup>6</sup> In this context, thiophene-1-oxides and thiophene-1,1-dioxides represent intriguing monomer units, given their electron-deficient nature. A recent study by Barbarella et al. demonstrated that introduction of thiophene-1,1-dioxide units into thiophene oligomers results in decreased electronic band gaps and higher electron affinities.<sup>7</sup> Theoretical studies on the electronic structures of poly(thiophene-1-oxide) and poly(thiophene-1,1-dioxide) predict that these materials should have lower band gaps than polythiophene but do not agree on which polymer would have the lowest band gap.<sup>8</sup> Here we report a versatile, high-yield synthetic procedure for thiophene-1-oxides and mixed thiophene-

thiophene-1-oxide oligomers. This methodology should prove useful for incorporation of thiophene-1-oxide units into a variety of oligomeric and polymeric structures.

In general, the zirconocene coupling of alkynes tolerates the presence of bromo-aryl functionalities and therefore provides convenient routes to difunctional building blocks that can be employed in carbon–carbon coupling routes to oligomers and polymers.<sup>9</sup> For example, the reaction of 4,4-bis(hexyloxymethyl)-1,7-bis-*p*-bromophenyl-1,6-heptadiyne with zirconocene, as generated by the Negishi method,<sup>10</sup> provides solutions of the zirconacyclopentadiene **1** in high yield. However, an attempt to prepare the thiophene monoxide **2c** (see eq 1) by the reaction of **1** with thionyl chloride gave only a 10% yield of the desired product, along with the corresponding thiophene (20%) and several unidentified side products.

Considerably better results were obtained by the two-step procedure outlined in eq 1. Generation of metallacycle **1** in THF gave a brown solution, through which SO<sub>2</sub> was bubbled to produce a bright yellow solution of the desired product **2c** within 10 min. Compound **2c** was isolated in 85% yield as yellow crystals after standard workup. The IR spectrum contains a characteristic  $\nu$ -(S=O) stretching band at 1043 cm<sup>-1</sup>, and the pyramidal nature of the sulfur atom manifests itself in inequivalent <sup>1</sup>H NMR shifts for the methylene protons of the fused, five-membered ring. Interestingly, the  $\lambda_{\text{max}}$  value for **2c** (388 nm) is red-shifted with respect to corresponding values for the thiophene (342 nm) and thiophene dioxide (378 nm).

Table 1 provides examples of other one-pot reactions that convert an alkyne or diyne to the corresponding thiophene-1-oxide by the method of eq 1. The yields for these reactions are



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generally quite high, indicating that oxo-transfer from the SO<sub>2</sub> reagent to zirconocene is quite efficient as compared to the analogous process with thionyl chloride, which gives Cp<sub>2</sub>ZrCl<sub>2</sub> as the final zirconium-containing product. Note that tetraphenylthiophene-1-oxide (**2a**, entry 1) is formed in very high yield, whereas the synthesis from thionyl chloride is reported to give yields of ~50–60%.<sup>4</sup> Zirconocene coupling of 3-hexyne followed by reaction with thionyl chloride gave only a trace of tetraethylthiophene-1-oxide (**2b**), while the reaction with SO<sub>2</sub> gave **2b** in excellent yield. Note that the few thiophene-1-oxides that have been successfully isolated feature sterically bulky substituents (e.g., Ph,<sup>2d,4</sup> SiR<sub>3</sub>,<sup>2c,11</sup> <sup>t</sup>Bu<sup>2a,c</sup>) that protect against decomposition reactions. Compound **2b** is reasonably stable at room temperature over several days as a pure oil, and only slight decomposition was noted for a chloroform-*d* solution after 4 days.

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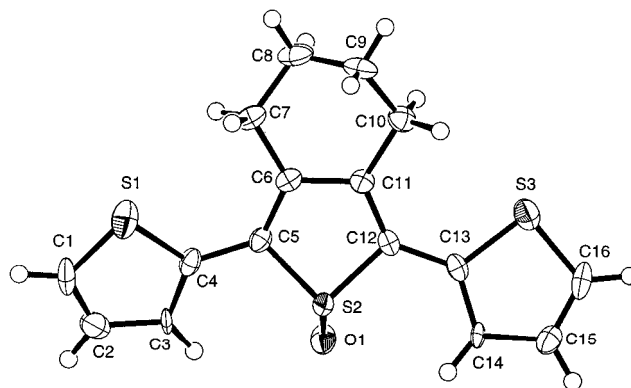
**Table 1.** Data for Thiophene-1-oxides Prepared from Various Alkyne Starting Materials

Entry	alkyne	product	yield	$\lambda_{\max}$ (nm)
1			95%	378
2	Et—C≡C—Et		85%	322
3			85%	388 (342, <sup>a</sup> 378 <sup>b</sup> )
4			92%	378
5			92%	388 (382 <sup>b</sup> )
6			50%	432 (428 <sup>b</sup> )
7			70%	428 (420 <sup>b</sup> )
8			70%	424 (366, <sup>a</sup> 416 <sup>b</sup> )
9			75%	492 (490 <sup>b</sup> )

<sup>a</sup>  $\lambda_{\max}$  value for the corresponding thiophene. <sup>b</sup>  $\lambda_{\max}$  value for the corresponding thiophene-1,1-dioxide.

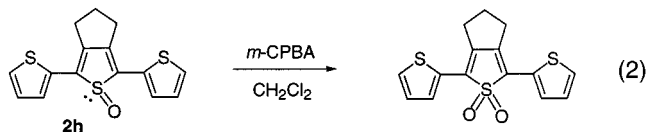
In addition to **2c**, the arylbromides **2d** and **2e** were obtained in high yield. Furthermore, this method appears to be quite useful in the efficient syntheses of mixed thiophene/thiophene-1-oxide oligomers (**2f–2i**).<sup>12</sup> All of the new thiophene-1-oxides in Table 1, except for **2b**, are stable at room temperature in air over periods of at least several weeks. As for **2c**, the  $\lambda_{\max}$  values for these oligomers are red-shifted with respect to those for the corresponding dioxides and (in the case of **2h**) the corresponding thiophene. The molecular structure of **2g** (Figure 1) consists of a central diene fragment, with C(5)–C(6), C(6)–C(11), and C(11)–C(12) distances of 1.357(6), 1.460(6), and 1.358(6) Å, respectively. As expected, the oxidized sulfur atom exhibits a pyramidal geometry and lies somewhat out of the C(5)–C(6)–C(11)–C(12) least-squares plane (by 0.23 Å). The latter plane forms dihedral angles with the substituent thiophene ring planes of 11.24° and 26.31°. It is interesting to compare the structure for an analogous di(thienyl)silole derivative, 1,1-dimethyl-3,4-trimethylene-2,5-di-(2-thienyl)silole, which possesses a five-membered ring fused to the silole ring. Although the latter compound has significantly lower dihedral angles between the thiophene and silole rings (6.14° and 10.55°), it has a higher energy absorption (409 nm, vs 428 nm for **2g**).<sup>13</sup>

(12) The lower yield for **2f** results from some debromination during its synthesis.



**Figure 1.** ORTEP diagram for **2g**. S(2)–O(1) bond distance, 1.495(3) Å; bond angles (deg), C(5)–S(2)–C(12) 91.0(2), O(1)–S(2)–C(5) 112.3(2), O(1)–S(2)–C(12) 112.1(2).

The synthesis of the first mixed thiophene-thiophene-1-oxide structures presented an opportunity to examine competing intramolecular oxidation reactions. This is of interest given previously reported attempts to prepare thiophene-1-oxides via the direct oxidation of thiophenes. It has been suggested that the difficulty with this approach lies in the greater sensitivity of the monooxide (vs the starting thiophene compound) toward oxidation, such that the main product is typically the thiophene dioxide.<sup>2,3</sup> In fact, we have found that this reactivity difference allows for selective oxidations of thiophene-1-oxide groups in the presence of thiophenes. Thus, the oxidation of **2h** by 1 equiv of *m*-chloroperbenzoic acid (*m*-CPBA) at room temperature gave the corresponding 1,1-dioxide in 78% isolated yield (eq 2).



Similarly, **2i** was converted to its corresponding thiophene-1,1-dioxide in 75% isolated yield. Thus, mixed thiophene-thiophene-1-oxide oligomers and polymers should serve as useful precursors to the corresponding thiophene-thiophene-1,1-dioxide structures.

In conclusion, we report here a general and efficient method for the synthesis of various functionalized thiophene-1-oxides derivatives, which have not been previously available. This method, based on oxo-transfer from sulfur dioxide to zirconocene, should allow us to investigate electronic properties for a variety of new oligomeric and polymeric structures incorporating thiophene-1-oxide units.

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**Supporting Information Available:** Detailed experimental procedures for the preparation and spectroscopic characterization of all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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