A Facile Approach to New Vinylogous Tetrathiafulvalene (TTF) Derivatives: 2,3-Bis(1,3-dithiole-2-ylidene)succinonitriles

Chunyang Jia, a Shi-Xia Liu,* a Antonia Neels, b Helen Stoeckli-Evans, b Silvio Decurtins* a
a Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, 3012 Bern, Switzerland
Fax +41(31)6313995; E-mail: decurtins@iac.unibe.ch
b Institut de Chimie, Université de Neuchâtel, Av. de Bellevaux 51, 2007 Neuchâtel, Switzerland

Received 22 December 2004; revised 29 March 2005

SYNTHESIS 2005, No. 13, pp 2157–2160
Advanced online publication: 13.07.2005
DOI: 10.1055/s-2005-869997; Art ID: T16004SS
© Georg Thieme Verlag Stuttgart · New York

Abstract: A new approach to vinylogous TTF derivatives 5 via an alkyne-coupling reaction is reported. Their fundamental redox behavior has been studied. A proposed reaction mechanism, which accounts for the formation of compounds 5 is discussed.

Key words: cycloadditions, substituent effects, sulfur, synthesis, vinylogous tetrathiafulvalene

Recently, vinylogous TTF derivatives 1 (Figure 1) have attracted considerable attention due to their highly electron-donating properties and reduced on-site Coulombic repulsion.1 They have been used as components for organic conductors and molecular devices (switches, motors, sensors, etc.).2 It is noteworthy that their redox behavior is dependent on the steric hindrance and donating (or withdrawing) character of R.1b,c

Figure 1

In general, there are two main strategies for the preparation of vinylogous TTF derivatives. On one hand, the most widely used methods are either the Wittig reaction of a (1,3-thiole-2-yl) phosphonium salt or the Wittig–Horner reaction of a phosphonium ester with an appropriate aldehyde.3 On the other hand, a variety of vinylogous TTF derivatives with different substituents such as alkyl and aryl groups at vinyl positions have been synthesized by intramolecular oxidative dimerization of substituted 1,4-dithiafulvenes.1b,c,d However, these methods show some drawbacks as tedious separations and multistep procedures. During our work it was discovered that 4,5-dicyano-1,3-thiole-2-thione and 4,5-dicyano-1,3-thiole-2-one were stirred at 120 °C in the presence of triethyl phosphate.6 Surprisingly, instead of the expected compound, a new vinylogous TTF derivative 5b was obtained, the structure of which was confirmed by its spectroscopic data such as NMR, MS, IR as well as X-ray structure analysis.7

Scheme 1

SYNTHESIS 2005, No. 13, pp 2157–2160
Advanced online publication: 13.07.2005
DOI: 10.1055/s-2005-869997; Art ID: T16004SS
© Georg Thieme Verlag Stuttgart · New York

To further study the versatility of this approach, analogous reactions were conducted with three other 4,5-dialkylthio-1,3-thiole-2-thiones (Scheme 1). After purification, the corresponding vinylogous TTF derivatives were obtained. All new compounds 5 have been characterized by IR, NMR spectroscopy, EI mass spectrometry.
and also elemental analyses as listed in the experimental section. The reaction procedure involving separation and purification is straightforward, but the yields are rather low. As a consequence, the reaction conditions were modified by exchanging triethyl phosphate with trimethyl phosphate or tri(isopropyl) phosphate as well as probing different reaction temperatures ranging from 80–120 °C. But in all cases there were no marked improvements on the yields.

However, the coupling reaction could be readily carried out under microwave-heated closed-vessel conditions without an inert atmosphere. For example, the reaction of 4,5-dimethylthio-1,3-thiole-2-thione with 4,5-dicyano-1,3-thiole-2-one was performed in three hours at 120 °C in a sealed microwave vessel on the same scale and gave 5b in a 26% yield, substantially improved compared to the open-vessel reaction. These results indicate also that the volatile intermediate dicyanoacetylene (3) is formed during the reaction. Therefore, the coupling reaction may proceed through the mechanistic pathway outlined in Scheme 1. Obviously, dicyanoacetylene (3) plays a crucial role in the formation of compounds 5. Through [2+2] cycloaddition of the triple bond of dicyanoacetylene (3) and the center double bond of TTF derivatives 2, cycloacetylene derivatives 4 are formed as intermediates, which are stabilized by electrocyclic ring opening to give compounds 5 (Scheme 1). Similar [2+2] cycloaddition reactions of dicyanoalkyne compounds and TTF derivatives have been reported by several groups.

It is noteworthy that 4,5-dicyano-1,3-thiole-2-one can not be pyrolyzed below a temperature of 500 °C to give dicyanoacetylene. In our case, the pyrolysis can proceed through a mechanistic pathway as illustrated in Scheme 2. Obviously, trialkyl phosphite plays an important role and promotes the formation of dicyanoacetylene (3). Furthermore, based on the above-mentioned experimental observation, it is essential to use sealed-vessel microwave heating technology. This can be explained by considering that dicyanoacetylene has high vapor pressure and therefore can be simply distilled off under the open-vessel conditions, giving rise to low yields of compounds 5.

The molecular structure of compound 5b is depicted in Figure 2. It has a non-planar structure with C2 symmetry as observed in the substituted TTF vinylogues. The dihedral angle between the two 1,3-dithiolemethylenetiorethene moieties is 91.7°. The molecular structure is also consistent with the spectroscopic and analytical data.

The electrochemical properties of compounds 5 in CH2Cl2 were investigated by cyclic voltammetry. As expected from the X-ray structure analysis, they all show reversible one-stage two-electron redox waves (Figure 3). This fact suggests that their cation radical states are thermodynamically unstable because of their non-planar structures, which is in good agreement with previously published results. It has been, however, pointed out that the TTF vinylogue skeletons can be planar and undergo two reversible one-electron oxidation when the substituents at the vinyl positions are twisted away from the π-conjugated framework. In the case of compounds 5, each cyano group is nearly coplanar with the adjacent 1,3-dithiole ring, forming two planes almost orthogonal to each other. Moreover, due to the very strong electron-withdrawing effect of cyano groups, the values of the oxidation potentials of compounds 5 are much higher than those of the analogues, indicating that they are weaker electron donors. For comparison, the oxidation potentials of bis(ethylenedithio)tetrathiafulvalene (ET) was also measured under the same conditions (Table 1).
Table 1 Oxidation Potentials of Compounds 5 and ET in CH₂Cl₂ (E₁/₂ in V vs Ag/AgCl, Pt Working Electrode with 0.1 M Bu₄NPF₆, 100 mV s⁻¹)

<table>
<thead>
<tr>
<th>Compound</th>
<th>E₁/₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>0.95</td>
</tr>
<tr>
<td>5b</td>
<td>1.05</td>
</tr>
<tr>
<td>5c</td>
<td>1.11</td>
</tr>
<tr>
<td>5d</td>
<td>1.07</td>
</tr>
<tr>
<td>ET</td>
<td>0.55</td>
</tr>
</tbody>
</table>

In summary, the outlined procedure provides a useful and straightforward pathway to the preparation of vinylogous TTF derivatives. Since the cyano group can offer a range of modifiable functionalities, this kind of vinylogous TTF derivatives might constitute promising building blocks for obtaining further novel π-electron donors. Finally, a possible mechanism for this new approach is discussed. Preventing removal of dicyanoacetylene from the reaction mixture by the use of a sealed-vessel microwave system leads to significantly enhanced yields.

All reactions were carried out under a dry N₂ atmosphere in an oven-dried round-bottomed flask. Chemicals were purchased from commercial sources and were used as received. TLC was carried out using aluminum sheets precoated with silica gel 60 F₂54. The plates were inspected under UV light (254 nm) and, if required, developed in I₂ vapor. Column chromatography was carried out using silica gel CH₂Cl₂–hexane (3:1) as eluent. Evaporation of the solvent under reduced pressure and chromatography of the residue on silica gel using CH₂Cl₂–hexane (3:1) as eluent afforded the products. The following compounds were thus obtained. The yields are given in the case triethyl phosphite was used.

5a Yellow powder; yield: 12%; mp 281–282 °C.

IR (KBr): 2924, 2184 (CN), 1440 cm⁻¹.

1H NMR: δ = 6.70–6.80 (m, 4 H).

13C NMR: δ = 81.7, 115.7, 122.9, 123.6, 168.0.

MS (EI): m/z (%) = 280 (100).

5b Yellow powder; yield: 13%; mp 214–215 °C.

IR (KBr): 2922, 2185 (CN), 1470, 1449 cm⁻¹.

1H NMR: δ = 2.46 (s, 6 H), 2.49 (s, 6 H).

13C NMR: δ = 19.1, 19.3, 84.5, 114.4, 129.6, 131.1, 163.1.

MS (EI): m/z (%) = 464 (100).

5c Yellow powder; yield: 15%; mp 270–271 °C.

IR (KBr): 2924, 2191 (CN), 1727, 1446 cm⁻¹.

1H NMR: δ = 3.35–3.36 (m, 8 H).

MS (EI): m/z (%) = 460 (30).

5d Yellow powder; yield: 28%; mp 90–91 °C.

IR (KBr): 2965, 2184 (CN), 1747, 1459 cm⁻¹.

1H NMR: δ = 0.99–1.06 (m, 12 H), 1.63–1.73 (m, 8 H), 2.81–2.88 (m, 8 H).

13C NMR: δ = 13.1, 23.1, 38.5, 38.6, 84.2, 114.5, 130.1, 131.2, 163.0.

MS (EI): m/z (%) = 576 (75).

5e Yellow powder; yield: 13%; mp 214–215 °C.

IR (KBr): 2922, 2185 (CN), 1470, 1449 cm⁻¹.

1H NMR: δ = 2.46 (s, 6 H), 2.49 (s, 6 H).

13C NMR: δ = 19.1, 19.3, 84.5, 114.4, 129.6, 131.1, 163.1.

MS (EI): m/z (%) = 464 (100).

Acknowledgment

The present research work was financially supported by the Swiss National Science Foundation (Project No. 200020-100432). We thank Prof. Philippe Renaud for helpful discussions about the reaction mechanism.

References


(7) Slow evaporation of the solution of 5b in CH2Cl2 gave single crystals suitable for X-ray diffraction measurement. Crystal data for compound 5b: C14H12N2S8, MW = 464. monoclinic, C2, a = 16.527 (2), b = 5.2211 (6), c = 12.897 (2) Å; β = 118.955 (13)°, V = 973.8 (2) Å³, T = 153 (2) K, Z = 2, D = 1.585 g·cm⁻³, µ = 0.917 mm⁻¹, λ = 0.71073 Å, F(000) = 476, independent reflections (Rint = 0.1017), 3870 reflections collected; refinement method, full-matrix least-squares refinement on F²; goodness-of-fit on F² = 0.761; Final R indices [I > 2σ(I)] R1 = 0.048, wR2 = 0.118.


