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Synthesis of the First 1,3-Ditellurole-Containing Radialene-Type TTF Derivatives

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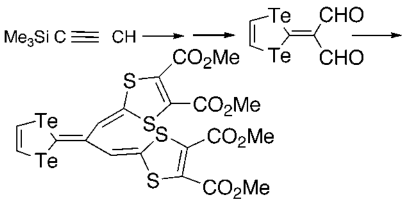
ABSTRACT

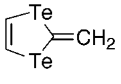


The first synthesis of dendralene-type TTF derivatives bearing a 1,3-ditellurole ring has been achieved. Preliminary electrochemical results are presented.

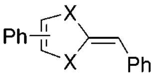
The report of one-dimensional conductivity in a complex formed from tetrathiafulvalene (TTF, **1**) and tetracyanoquinodimethane (TCNQ, **2**) has triggered tremendous synthetic activity in this area.[1] The work has led to the replacement of the sulfur atoms by selenium and tellurium, as well as the synthesis of vinylogs, extended TTFs, heterocycle spaced TTFs, and dendralene-type TTF derivatives. Recently, the first 1,3-diselenole containing dendralene-type TTF derivatives (**3**−**5**) were reported from our laboratory.[2]

The basic starting material and synthetic route for these molecules was 2-methylene-1,3-diselenole **6**[3] as shown in Scheme 1.

The tellurium analogue of **6**, viz. **8**, has been reported in 1% yield from the reaction of acetylene and tellurium in the presence of reducing agents[4]. Obviously, a better route to this simple heterocycle was in order. The base-catalyzed decomposition of selenadiazole to give **6** was not applicable because 1,2,3-telluradiazole is not known. The alternate protocol involved the protonation of an ethynyl tellurolate by analogy to the synthesis of the 2-benzylidene-1,3-diselenole **9** and its tellurium analogue **10**.[5a,b]



8



9 X=Se

10 X=Te

Accordingly, trimethylsilylacetylide was reacted with tellurium and the resulting tellurolate was protonated to give **11**. Unfortunately, ditellurole **11** could not be obtained analytically pure, suffering extensive decomposition during purification, nor could it be desilylated to **8**. However, the crude material was subjected to the Vilsmeier−Haack reaction to give the required dialdehyde **12** (Scheme 2).

Dialdehyde **12** behaved normally as seen by its ready condensation with malononitrile and carbomethoxymethyl phosphorane to give **13** and **14**, respectively, in 45% and 70% yields. In like fashion, 4,5-dicarbomethoxy-1,3-dithiole

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[1] Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1996**, *18*, 1.

[2] Amaresh, R. R.; Liu, D.; Konovalova, T.; Lakshmikantham, M. V.; Cava, M. P.; Kispert, L. D. *J. Org. Chem.* **2001**, *66*, 7757.

[3] Jackson, Y. A.; White, C. L.; Lakshmikantham, M. V.; Cava, M. P. *Tetrahedron Lett.* **1987**, *28*, 5635.

[4] Amosova, S. V.; Potapov, V. A.; Bulakhova, Z. A.; Romanenko, L. S.; *Sulfur Lett.* **1991**, *13*, 143.

[5] (a) Mayer, R.; Hunger, B.; Prousa, R.; Müller, A. K. *J. Prakt. Chem.* **1967**, *35*, 294. (b) Lakshmikatham, M. V.; Cava, M. P.; Albeck, M.; Engman, L.; Wudl, F.; Aharaon-Shalom, E. *J. Chem. Soc., Chem. Commun.* **1981**, 828.

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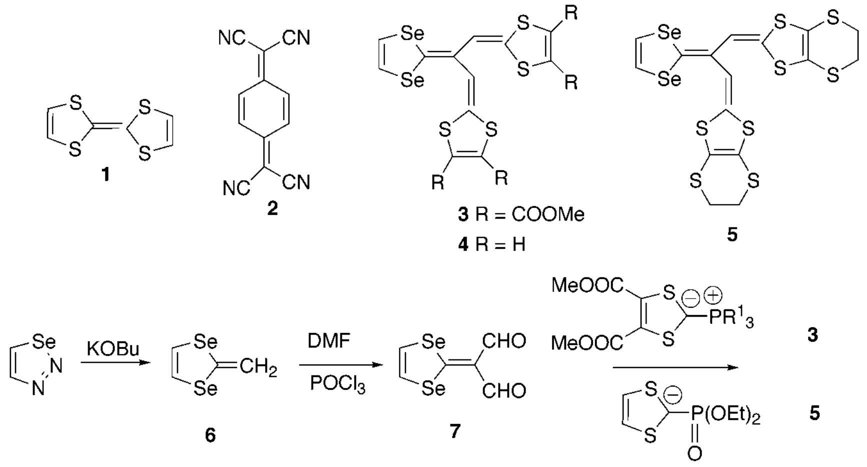
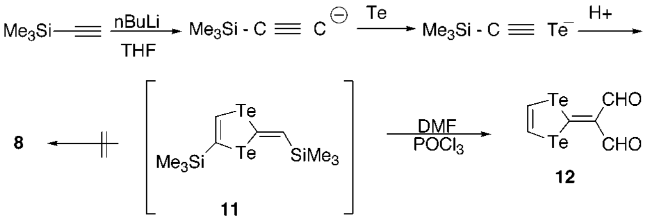
Scheme 1



phosphorane condensed readily in the presence of sodium hydride to give the dendralene **15** in 63% yield. The phosphonates **16** and **17** gave the dendralenes **18** and **19** in 38% and 43% yields, respectively, upon condensation with dialdehyde **12** in the presence of base. (Scheme 3)

Scheme 2



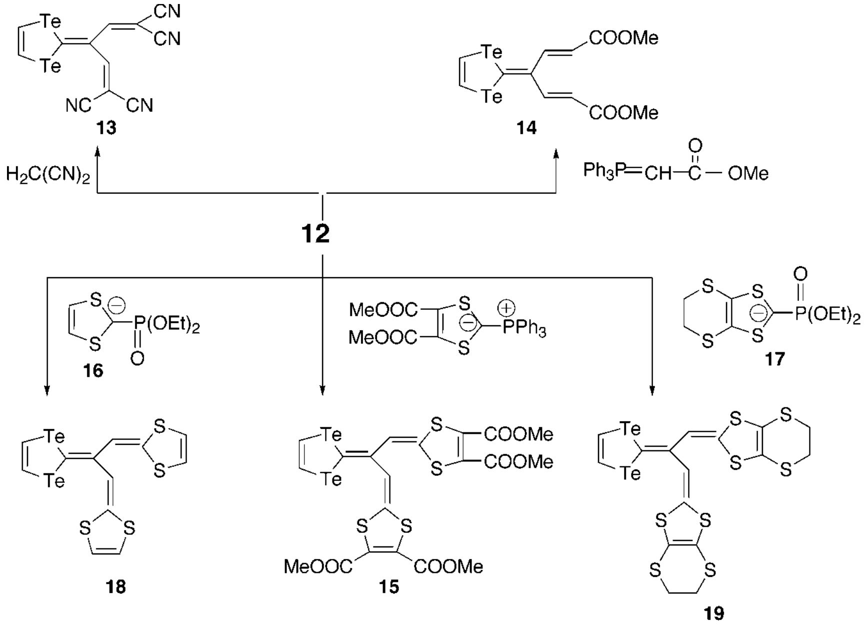
Cyclic Voltammetry. CV data (Table 1) were determined in CH_2Cl_2 containing TBAHFP. Dendralene **15** exhibited three anodic waves at 0.464, 0.633, and 1.53 V referenced

Table 1. CV Data (V) in 0.1 M TBAHFP in CH_2Cl_2

compd	P_a^1	P_a^2	P_a^3	P_c^4	P_c^5	P_c^6	P_c^7
15	0.464	0.633	1.53	1.199	0.495	0.314	
18	0.228	0.409	1.104	1.733[a]	0.856	0.094	
19	0.287	0.483	1.112	1.309[a]	1.757[a]	1.729	0.165

[a] Anodic peaks P_a^4 and P_a^5.

Scheme 3



to the calomel electrode. Three cathodic waves were noted at 1.199, 0.495, and 0.314 V. Clearly the last oxidation potential was not reversible. The peak differences between the corresponding anodic and cathodic potentials are 150 and 138 mV for the first and second oxidation potentials. When compared to the values of the corresponding diselenole analogue **3**, the first oxidation to the radical cation in **15** occurs, not surprisingly, at a lower potential, −0.109 V lower than that for **3** under the same conditions.

Furthermore, the differences between the peak potentials of the anodic and corresponding cathodic scans in **3** are 61 and 64 mV compared to 150 and 138 mV in **15**.[2]

Similarly the CV of **18** exhibited three anodic oxidation waves at 0.228, 0.409, and 1.104 V, but the corresponding cathodic waves were not sharp. Two humps were noted at 1.733 and 0.856 V and a peak at 0.094 V.

Dendralene **19** was very insoluble, but the CV of a very dilute solution showed five anodic peaks at 0.287, 0.483, 1.112, 1.309, and 1.757 V. The cathodic peaks were broad with one at 1.729 V and another at 0.165 V.

The behavior of **18** and **19** is again not quite comparable to the corresponding selenium compounds **4** and **5**. The trend toward a lower oxidation potential is explicable. The anodic and cathodic potentials at the first two oxidation levels are reproducible, but the difference between P_a and P_c is >60 mV, one of the criteria for reversibility or quasireversibility. Extensive electrochemical investigations will be needed to understand the properties of the 1,3-ditellurole containing dendralene-TTF molecules. There is also another aspect to be considered. Many years ago Bender et al. studied the 1,3-ditellurolium cation in detail.[6] Almost 20 years ago, the authors demonstrated that the simple 1,3-ditellurolium cation was stable at −30 °C but rearranged slowly to the unstable 1,2-ditellurolium ion at room temperature. The CV of 1,3-ditellurole was reported in 1985.[7] The first oxidation potential at 0.64 V was reversible, whereas the second wave at 1.12 V was irreversible, suggesting that the radical cation was relatively stable compared to the second species generated. The identity of this second oxidation species is unknown. Our observations on the electrochemistry of the dendralene-type TTF derivatives incorporating the 1,3-ditellurole moiety appear to parallel the observations on the simple parent.

In conclusion, we have demonstrated a viable synthesis of the ditellurole containing dendralene-TTF molecules and drawn attention to the differences in the electrochemical behavior of such compounds.

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Supporting Information Available: Experimental details, NMR spectra, and cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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