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# Synthesis and transformations of some new 2,4-bismethylene-1,3-ditelluretanes

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Abstract—A novel four-membered 1,3-ditelluretane dialdehyde 8/9 was synthesized from trimethylsilylethynyl tellurolate. The dialdehyde was transformed into extended tetrathiafulvalenes (14 and 15). These are the first examples of ditelluretane spaced TTF derivatives. © 2003 Elsevier Science Ltd. All rights reserved.

A number of 1,3-dithietane derivatives 1 have been synthesized via several approaches but mainly by the reaction of carbon disulfide with anions derived from active methylene derivatives.<sup>1</sup> In contrast, only three examples of 1,3-diselenetane are known.<sup>2</sup> These were obtained when selenaketenes produced in a matrix by pyrolysis of selenadiazoles were warmed up. The only 1,3-ditelluretane to have been unambiguously characterized via X-ray was the 2,4-bis benzylidene derivative **3**.<sup>3,4</sup> Petrov et al. have also reported the formation of 1,3-ditelluretanes **3** (R=H, R=Me).<sup>5</sup> It should be noted that these arylidene ditelluretanes are not generally amenable to further transformations.

Ditelluretane 3 (R = H) was obtained as a very minor bye-product along with *cis/trans* 1,3-ditellurafulvene 4 from the reaction of phenylacetylide with tellurium followed by acidification with trifluoroacetic acid (Scheme 1). This reaction has no parallel in the case of



## Scheme 1.

sulfur or selenium, where four-membered rings were not detected.

In the course of our investigations on the synthesis of 1,3-ditellurole-containing radialene-type TTF derivatives,<sup>6</sup> it was observed that depending on the protonsource and conditions of protonation of the trimethylsilylethynyl tellurolate anion, either the ditellurafulvalene or the 1,3-ditelluretane derivative can be generated *selectively*. Thus, the use of *t*-butanol at room temperature furnished the ditellurafulvene **5** whereas the use of trifluoroacetic acid in *t*-butanol at  $-20^{\circ}$ C led to the formation of ditelluretane **7** presumably via the telluraketene **6** (Scheme 2).



*Keywords*: 1,3-ditelluretane dialdehyde; tellurium; Horner–Wittig reaction. \* Corresponding author.

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Scheme 2.



Figure 1. X-Ray structure of *trans*-bis-2,4-formylmethylene-1,3-ditelluretane (8).

The use of ethereal hydrogen chloride did not furnish the telluretane 3 (R=H) exclusively.

Although 5 is reported in the literature,<sup>7</sup> we were unable to isolate it. However, as in the case of 5, Vilsmeier–Haack reaction on the crude ditelluretane 7 furnished a mixture of *trans* and *cis* dialdehydes 8 and  $9^8$  in 10% yield (Scheme 2). Their separation proved to be tedious and involved chromatography via multiple development on the Chromatotron to isolate small samples of the pure compounds.

Both dialdehydes 8 and 9 crystallized readily. However, only the crystals of the *trans* isomer 8 were suitable for X-ray analysis. The crystal structure revealed that 8 is planar, with the aldehyde groups oriented in the *trans* configuration relative to the ditelluretane ring (Fig. 1). The crystal packing down the crystallographic axis b revealed the formation of columns through  $\pi$ - $\pi$  stacking interactions. The distance between molecules in the columns was 6.41 Å. The crystal packing down the crystallographic axis c revealed that the columns were arranged in a herring-bone fashion. The distance between the molecules in the herring-bone was 4.081 Å.

In view of the difficulties associated with the separation of the *cis* and *trans* isomers of the dialdehyde, subsequent Wittig reactions were carried out on the aldehyde mixture (8/9). Therefore all the products are E/Z mixtures. The stable phosphorane 10 condensed smoothly with 8/9 to give E/Z diester product 11.<sup>9</sup> Diesterdithiole phosphorane 12 derived from the corresponding phosphonium salt,<sup>10</sup> as well as the ylid from the dithiolephosphonate 13<sup>11</sup> condensed smoothly with the aldehyde mixture to give 14,<sup>12</sup> and 15,<sup>13</sup> the first examples of vinylogous TTF derivatives separated by a 1,3-ditelluretane moiety (Scheme 3). Some years ago, the synthesis of vinylogous TTF derivatives bearing a heterocyclic spacer of the type **16** was reported.<sup>14</sup> The major difference between **16** and the present ditelluretane-separated TTF derivatives lies in the fact that in the former, the dithiole units are separated by four double bonds whereas in the latter, the ditelluretane is equivalent to one double bond in addition to the four double bonds. It can also be considered to be the equivalent of a cyclohexadiene unit. No such TTF derivative is reported in the case of the dithietane and diselenetane series. New approaches have to be devised so as to make these compounds available for direct comparison with the ditelluretane derivatives.



Solutions of ditelluretane **15** were extremely sensitive to laboratory conditions. Therefore, cyclic voltammetry was carried out on the ditelluretane derivative **14**. The cyclic voltammogram of **14** showed anodic peaks at 507.1, 715.4, 834.8 and 1318 mV. Only the first oxidation peak was reversible with the corresponding cathodic peak at 480.2 mV, the difference being 26.9 mV. This behavior is in contrast to that exhibited by the vinylog **16** (X=O, NMe and S),<sup>14</sup> all of which show two well resolved reversible waves (Table 1).

No conclusions can be drawn from this result because of the basic difference between 16 and 14.

The major difference between 14 and 16 lies in the species generated during the second oxidation step. The latter generates a radical cation in the first step and a dication during the second oxidation step. In contrast, in the case of 14 the second step can lead to the formation of a diradical dication (Scheme 4).

The propensity of tellurium centered radical ions and cations in five-membered 1,3-ditellurole rings is well documented.<sup>15,16</sup> This is the first example of a cyclic voltammogram of a functionalized 1,3-ditelluretane. It will obviously involve synthesis of more 1,3-ditelluretane derivatives and extensive electrochemical analysis to fully understand the behavior of such ion-radicals.



Scheme 3.

Table 1. Oxidation potentials<sup>a</sup> of 14 and 16

Compound	$P_{\rm a1}$ rev.	P <sub>a2</sub>	$P_{a3}$ irr.	$P_{a4}$ irr.	$P_{c1}$ rev.
14	507.1 mV	715.4 mV irr.	834.8 mV irr.	1.318 V irr.	480.2 mV
16 (X = NMe)	480.0 mV	810 mV rev.			
16 (X=S)	690 mV	790 mV			
16 (X=O)	580 mV	710 mV rev.			

<sup>a</sup> 0.1 molar solution in CH<sub>2</sub>Cl<sub>2</sub> containing TBAHFP, Pt W.E. referenced to SCE.



### Scheme 4.

*Summary*. Preliminary work is presented on the synthesis, and X-ray of the first formyl substituted 1,3-ditelluretane. Vinylogous TTF derivatives bearing the 1,3-ditelluretane spacer are described. Cyclic voltammetry on one of these vinylogs is presented.

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- 8/9 mixture: mp 161–169°C (dec.), NMR spectrum, δ 10.34, s, 10.27, s (1H each), 8.32, s, 8.18, s (1H each); mass spectrum: m/z 368 (M<sup>+</sup>, 62%), 340 (80), 256 (100), 184 (28), 156 (42), 130 (48). 8, red-orange crystals, mp 167–174°C; NMR spectrum, δ 10.27 s (2H), 8.18 s (2H).

Crystal data for **8**: C<sub>3</sub>H<sub>2</sub>OTe, 181.65, monoclinic, space group P2(1)/n, a=7.827(3), b=6.141(2), c=8.247(3) Å,  $\beta=99.380$  (7)°, V=391.1(3) Å<sup>3</sup>, Z=4,  $D_{calcd}=3.085$  g cm<sup>-3</sup>,  $R_1=0.0456$ ,  $wR_2=0.1178$  ( $I>2\sigma(I)$ ). Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication number CCDC 193652. A copy of the data can be obtained free of charge, from CCDC, 12 Union Road, Cambridge CB2 1EZ, [fax: +44(0) 1223-336033 or email: deposit@ccdc.cam.ac.uk].

- E/Z. 11: dark brown, mp 182–187.7°C; NMR spectrum, δ 7.70–7.62, 2d, (2H, J=10.4 Hz) 6.56–6.45, 2d, (2H, J=10.0 Hz), 5.57–5.47, 2d (2H, J=14 Hz), 3.83, 3.75, 2s (6H); mass spectrum: m/z 480 (M+, 22%), 476 (37), 240 (100), 212 (55), 155 (15), 119 (28).
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- E/Z 14: Brown solid, mp 157°C (dec.); NMR spectrum: δ 7.26, 7.06 d (2H, J=10.0 Hz), 5.18–5.10, 2d (2H, J=10.0 Hz), 3.82, 2s (6H); mass spectrum: m/z 768 (30%), 578 (40), 486 (100), 428 (20), 219 (37).
- 13. E/Z 15: Brown turning dark on exposure to light, mp 194°C (dec.); NMR spectrum: δ 7.55, 7.50, 2d (2H, J=10.4 Hz), 6.64–6.51, 2d (2H, J=10.6 Hz), 5.58, 5.53, 2s (4H); mass spectrum: m/z 540 (M+15%), 452 (53), 312 (12), 254 (83), 122 (31).
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