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STABILIZATION OF 1,2-DITELLUROLANE BY 2,3,5,6-TETRAMETHYLNITROSOBENZENE (NITROSODURENE)

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1,2-Ditellurolane is an extremely unstable heterocyclic compound which can be maintained in solution in the presence of nitrosodurene for several days. It is proposed on the basis of UV spectroscopy and ^1H NMR spectroscopy that a complex is formed which determines the stability of 1,2-ditellurolane. It is shown that stabilized 1,2-ditellurolane can be used in organic synthesis.

Keywords: 1,2-ditellurolane, nitrosodurene, complex with charge transfer.

Recently we presented a sufficiently simple method for the synthesis of the highly strained heterocyclic compound, 1,2-ditellurolane **1** [1]. The method is based on the reaction of elemental tellurium with 1,3-dihalopropane in hydrazine hydrate and base with subsequent treatment of the organic solution on the poly(trimethyleneditelluride) **2**. A radical pathway for the formation of compound **1** from the oligomer **2** was proposed on the basis of EPR data [1]. The solutions obtained were extremely unstable (especially in light and in the presence of traces of moisture) and 1,2-ditellurolane **1** is completely converted into 1,3-propaneditelluric acid in a few minutes.

Taking into account the proposed radical pathway for the formation of heterocycle **1** and also the possible radical pathway for its oxidative destruction, we have investigated the behavior of 1,2-ditellurane in the presence of the spin trap, nitrosodurene **3**. Capture by nitrosodurene **3** of the products of the decomposition of tellurium centered radicals (in particular, the formed organic radicals) was used for the indirect confirmation of the generation of $RTe^{\cdot}$, which are difficult to trap [2, 3]. In the course of our ESR studies no spin adducts of radicals with nitrosodurene **3** were isolated, however unexpectedly it was found that the blue color of solution, explained by the presence of 1,2-ditellurolane **1**, remained for several days in the presence of compound **3**.

To explain this observation the UV absorption spectra of 1,2-ditellurolane in chloroform and of the same solution in the presence of nitrosodurene **3** were studied. In the 500-800 nm region ditellurolane has two overlapping absorption bands at 561 and 654 nm. In the presence of compound **3** bathochromic shifts of 7 nm were observed for both absorption bands of ditellurolane **1**. Nitrosodurene **3** does not absorb in this spectral

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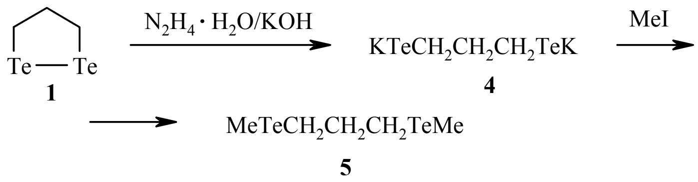
region, but it has a short wavelength absorption in chloroform at 309 nm. Previously the authors investigated the characteristics of the most stable isomer of 1,2-ditellurolane *via* a quantum-chemical study using DFT(B3LYP)/LanL2DZ within the PCM polarizable continuum model which showed that the medium had no effect on the total energy, vibration spectrum, and spatial structure over the ε = 1-78 range [1]. This permitted the attribution of the change in the spectral characteristics of 1,2-ditellurolane **1** in the presence of nitrosodurene **3** to intermolecular bonding with the nitrosodurene molecule which facilitates stabilization of the 1,2-ditellurolane ring.

Stabilization of 1,2-ditellurolane **1** with nitrosodurene **3** allowed the recording for the first time of the ^{125}Te and ^{13}C NMR spectra of the solution, in addition to the ^{1}H NMR spectrum [1]. In the ^{125}Te NMR spectrum there was a single resonance at 138.60 ppm in the form of a quintet with $^{2}J_{\text{H-C-Te}}$ = 28.4 Hz. The chemical shift observed corresponds to the chemical shift of aliphatic ditellurides, most of which are observed in the 49-166 ppm region [4].

In the ^{13}C NMR spectrum there are, apart from signals corresponding to nitrosodurene, two signals at 9.16 and 44.84 ppm assigned to resonances of the CTe and $\text{C}\underline{\text{C}}\text{C}$ carbons of the ditellurolane ring.

The possibility of stabilizing 1,2-ditellurolane **1** with nitrosodurene **3** permits the broadening of the use of compound **1** in the synthesis of tellurium-containing compounds used, in particular, as ligands for complex formation [5]. With the use of a solution of compound **1** in chloroform, in the presence of compound **3**, we have succeeded in the synthesis of 1,3-bis(methyltelluranyl)propane **5**. Under the influence of the hydrazine hydrate-KOH system, the Te–Te bond of compound **1** is split to give the ditellurolate **4**, methylation of which gave compound **5**.



So we have found a method for the stabilization of 1,2-ditellurolane **1**, which is unstable to oxidation, *via* its reaction with a solution of nitrosodurene **3**. In the presence of a spin trap – nitrosodurene **3** – the possibility of radical splitting of the Te–Te bond has been confirmed, which was not recorded in 1,2-ditellurolane.

EXPERIMENTAL

IR spectra of products in KBr tablets were recorded with a Bruker IFS-25 apparatus. UV spectra were recorded on a UV-vis Lambda 35 spectrometer ($CHCl_3$ solution, d = 1 cm). ^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded with a Bruker DPX-400 instrument (400, 100, and 126 MHz respectively) with HMDS as internal standard for ^{1}H and ^{13}C, and Me_2Te for ^{125}Te. EPR spectra were recorded with a Radiopan SE/X-2547 spectrometer equipped for high frequency measurement and with a magnetometer.

Poly(trimethyleneditelluride) 2. Powdered tellurium (12.8 g) was added at 75°C over 1 h to a solution of KOH (5.6 g) in hydrazine hydrate (40 g). The reaction mixture, which became a deep-claret color, was kept for 2 h at 80-90° and then cooled to 25°. Then 1-bromo-3-chloropropane (7.87 g) was added over 1.5 h. The mixture was kept for 2 h at 60-65°C, cooled, and the tellurokol which precipitated as a black sticky mass was isolated, washed with water, ethanol, and ether, and dried. Yield 14.1 g (94.6% based on tellurium used). IR spectrum, cm^{-1}: 2958, 2915, 2855 (ν CH_2); 1476, 1463, 1426, 1413, 1400 (δ_s CH_2); 1329, 1302, 1271, 1249

(ρ_ω CH_2, ρ_t CH_2): 1199, 1168, 1118, 906, 895, 788, 756, 694, 659, 627, 476, 420 (ν CC, ν CTe). Found, %: C 11.59; H 2.14; Hal 2.09; Te 83.44. Molecular mass (calculated from residual halogen – end-group analysis) 5530 units. C_3H_6Te (basic unit of tellurokol **2**). Calculated, %: C 12.11; H 2.02; Te 85.87.

The tellurokol **2** was paramagnetic and gave an EPR spectrum consisting of a broad intense singlet (29 mTl) with a *g*-factor of 2.011.

The solution of 1,2-tellurolane obtained from the oligomer **2** together with its ^1H NMR spectrum, have been described earlier [1].

Interaction of a Mixture of Nitrosodurene 3 and Chloroform on Tellurokol 2. A freshly prepared solution nitrosodurene **3** (0.01 g) in $CDCl_3$ (1 ml) was added to tellurokol **2** (0.12 g), the blue solution of 1,2-ditellurolane **1** was decanted and its ^1H (see [1]), ^{13}C, and ^{125}Te NMR spectra were recorded. The ^1H NMR spectra recorded after two days was identical to the previous spectrum.

1,3-Bis(methyltelluranyl)propane 5. A chloroform solution (10 ml) containing nitrosodurene **3** (0.1 g, 0.60 mmol) and 1,2-ditellurolane **1** (0.08 g, 0.27 mmol) was added dropwise with stirring to a solution of KOH (1.8 g, 32 mmol) in hydrazine hydrate (100 mmol) at 50-55°C. After completion of the addition, a solution of methyl iodide (0.075 g, 0.53 mmol) in chloroform (2 ml) was added. The chloroform layer was separated and analyzed. According to GLC (method of standard additions) the solution contained 0.7 g (80% yield) of compound **5**.

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