Synthesis of (*E*)-2-chlorovinyltellurium trichloride and (*E,E*)-bis(2-chlorovinyl) ditelluride

*V. A. Potapov, M. V. Musalova, and S. V. Amosova**

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 41 9346. E-mail: amosova@irioch.irk.ru

The reaction of tellurium tetrachloride with acetylene in CCl_4 at atmospheric pressure and ambient temperature affords earlier unknown (*E*)-2-chlorovinyltellurium trichloride in 30% yield, whose reduction with sodium bisulfite gives (*E,E*)-bis(2-chlorovinyl) ditelluride in 64% yield.

Key words: acetylene, tellurium tetrachloride, 2-chlorovinyltellurium trichloride, bis-(2-chlorovinyl) ditelluride, electrophilic addition, reduction, organotellurium compounds.

The compounds containing the vinyltelluro group find use in modern organic synthesis,[1] particularly, in cross-coupling and transmetallation reactions. It is known that reactions of tellurium tetrachloride with substituted acetylenes proceed as *syn*-addition, giving *Z*-configured products.[2,3] An example of the stereospecific *anti*-addition of tellurium tetrachloride to the triple bond is the reaction with unsubstituted acetylene[4] (pressure 12 atm, $CHCl_3$, 20—40 °C) giving (*E,E*)-bis(2-chlorovinyl)tellurium dichloride (**1**) in 62% yield (Scheme 1).

In the present work we found that the reaction of tellurium tetrachloride with acetylene in tetrachloromethane at atmospheric pressure and ambient temperature (passing of C_2H_2 for 3 h) resulted in the selective formation of earlier unknown (*E*)-2-chlorovinyltellurium trichloride (**2**) (30% yield, see Scheme 1). No formation of bisadduct **1** is observed under these conditions. The reaction proceeds stereospecifically as *anti*-addition and affords exclusively the *E*-isomer of compound **2**.

Compound **2** is also formed when the reaction is carried out under atmospheric pressure in a chloroform solution (^{1}H NMR monitoring in $CDCl_3$); however, under these conditions, compound **2** adds to the second acetylene molecule and transforms into dichloride **1**. Compound **2** is formed at the initial period of the reaction and then dichloride **1** appeared, whose content increases with time while the fraction of compound **2** gradually decreases.

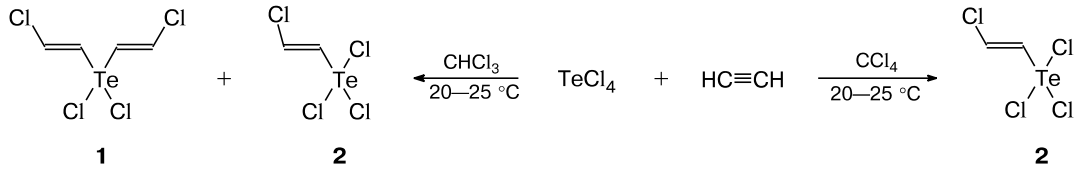
The reduction of compound **2** with sodium bisulfite affords earlier unknown (*E,E*)-bis(2-chlorovinyl) ditelluride (**3**) in 64% yield (Scheme 2).

The structures of compounds **2** and **3** were proved by ^{1}H and ^{13}C NMR spectroscopy and confirmed by the mass spectrometry (for ditelluride **3**) and elemental analysis data. The spin-spin coupling constants of the olefinic protons in the ^{1}H NMR spectra of products **2** and **3** (13.4 and 13.6 Hz) are typical of the compounds containing the *E*-configured ClCH=CHTe group.[4]

There are a few examples for the synthesis of vinyltellurium trichlorides[3]; however, data in the synthesis of these compounds from acetylene are lacking. The known examples for the synthesis of divinyl ditellurides concern the oxidation of vinyltellanylmagnesium halides or sodium vinyltellurolate.[5]

To sum up, a convenient stereospecific method for the preparation of products **2** and **3**, which are promising starting substances for the synthesis of new organotellurium compounds, from the accessible starting materials (acetylene and tellurium tetrachloride) was proposed.

Scheme 1



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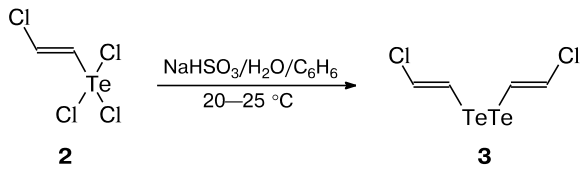
Scheme 2



2 **3**

Experimental

^{1}H (400.13 MHz) and ^{13}C (100.61 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer (HMDS as internal standard). The mass spectrum was obtained on a GCMS-QP5050A Shimadzu spectrometer (EI, 70 eV).

Tellurium tetrachloride was obtained from tellurium and sulfuryl chloride using a known procedure.[6]

(*E*)-2-Chlorovinyltellurium trichloride (2). Dry acetylene was bubbled through anhydrous CCl_4 (50 mL) for 1 h at ~20 °C, after which $TeCl_4$ (0.54 g, 2 mmol) was added to the solution, and the bubbling was continued for 2 h with vigorous magnetic stirring of the suspension. The solution was decanted, anhydrous CCl_4 (50 mL) was added to the precipitate, and the mixture was stirred for 1 h at ~20 °C. The liquid was decanted from the precipitate and combined with the first portion of a CCl_4 solution. The mixture was filtered, and CCl_4 was distilled off from the filtrate. The residue was product **2**: a colorless powder that darkened on heating to 45—47 °C and then decomposed. The yield was 0.18 g (30%). Found (%): C, 7.98; H, 0.78; Cl, 47.66. $C_2H_2Cl_4Te$. Calculated (%): C, 8.13; H, 0.68; Cl, 48.00. ^{1}H NMR (DMSO-d_6), δ: 7.38 (d, 2 H, CHCl, J = 13.4 Hz); 7.82 (d, 2 H, TeCH, J = 13.4 Hz). ^{13}C NMR (DMSO-d_6), δ: 131.32 (CHCl), 145.67 (TeCH).

(*E*,*E*)-Bis(2-chlorovinyl) ditelluride (3). A solution of sodium bisulfite obtained from $Na_2S_2O_5$ (0.95 g, 5 mmol) and water (5 mL) was added to a solution of compound **2** (0.15 g, 0.5 mmol) in benzene (2 mL). The mixture was purged with argon and stirred for 24 h at ~20 °C under argon. The mixture was extracted with benzene (3×5 mL), the organic phase was dried and filtered, and benzene was distilled off. Ditelluride **3** as a dark red oil was isolated by column chromatography on silica gel (eluent hexane). The yield was 60.8 mg (64%). Found (%): C, 13.08; H, 1.20; Cl, 19.06. $C_4H_4Cl_2Te_2$. Calculated (%): C, 12.70; H, 1.07; Cl, 18.75. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 6.49 (d, 2 H, CHCl, J = 13.6 Hz); 7.37 (d, 2 H, TeCH, J = 13.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 93.28 (TeCH), 125.34 (CHCl). MS, m/z (I_{rel} (%)): 380 $[M]^{+\bullet}$ (64), 319 $[M - C_2H_2Cl]^+$ (16), 293 $[Te_2Cl]^+$ (27), 258 $[Te_2]^{+\bullet}$, 252 $[M - Te]^{+\bullet}$ (47), 191 $[TeC_2H_2Cl]^+$ (100), 165 $[TeC_2H]^+$ (88), 130 $[Te]^{+\bullet}$ (80), 87 $[C_4H_4Cl]^+$ (18), 61 $[C_2H_2Cl]^+$ (44), 51 $[C_4H_3]^+$ (33).

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