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Dedicated to the 90th Anniversary of Academician M.G. Voronkov

Synthesis and Reductive Splitting of Tellurium-Containing Oligomers on the Basis of 1-Bromo-2-methyl-3-chloropropane

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Abstract—The results of the synthesis of tellurium-containing oligomers based on 1-bromo-2-methyl-3-chloropropane are presented. By the example of the reductive splitting of tellurocol the possibility is demonstrated of the synthesis of methyltellanyl derivatives, which are valuable reagents for organic synthesis and for the design of coordination compounds.

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Polymers and oligomers containing tellurium atoms in the chain possess a number of practically valuable properties [1]. Generally, they are synthesized by polycondensation of organic dihalogenides with polytellurides of alkali metals M_2Te_n (M = Na, K; n = 1–3), which, in turn, are prepared from elemental tellurium in the redox systems [2]. By using such an approach, polyaryleneditellurides have been prepared [3].

We prepared tellurium-containing oligomers with paramagnetic properties [4] from 1-bromo-3-chloropropane [5] and chlorex [6]. However, in the reaction of 1,2-dihaloethanes with tellurium (or selenium) under similar conditions no oligomeric products are formed, but rather dehalogenation with the evolution of ethylene and elemental chalcogens is observed [7]. A similar course of the reaction, that is, elimination of the vicinal halogen atoms (as halogenide anions) under the action of soft nucleophiles, in particular, chalcogen-containing, is a well-known reaction [8] proceeding, as many authors believe, as a halogenophilic attack of the nucleophile at the halogen atom [9]. The halogenophilic attack and the subsequent elimination of the halogen, in turn, are to a considerable extent determined by steric effects caused by the vicinal arrangement of the halogen atoms.

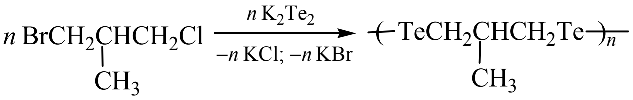
In some cases the elimination of halogens may occur also with the derivatives of 1,3-dihalopropanes. Thus, the course of the reaction of 1,3-dibromo– and 1,3-dichloropropane with RTeLi (R = Me, Ph) depends on the temperature: at –196°C the substitution of the halogen atoms by RTe is observed, whereas at 25°C, the formation of propene and R_2Te_2 [10]. The reaction of MeTeLi with tetrakis(bromomethyl)methane, in which the bromine atoms are in the 1,3-position to each other, the substitution of two bromine atoms by the methyltellanyl group is observed with elimination of the other two bromine atoms and the formation of the cyclopropane derivative [10].

1-Bromo-2-methyl-3-chloropropane (**I**) has the methyl group in the vicinal position with respect to the halogen atoms. The methyl group is sterically equivalent to the bromine atom [11], so, it can create steric hindrances to conventional nucleophilic substitution and favor the halogenophilic attack and elimination of the halogen atoms.

We have performed the reaction of dihalogenide **I** with elemental tellurium in the system hydrazine hydrate–KOH, in which tellurium suffers reductive activation with the formation of potassium telluride and polytellurides; for the ratio Te:KOH = 1:1, K_2Te_2 is predominantly formed [2].

$$4\,\mathrm{Te} + 4\,\mathrm{KOH} + \mathrm{N_2H_4{\cdot}H_2O} \rightarrow 2\,\mathrm{K_2Te_2} + \mathrm{N_2} + 5\,\mathrm{H_2O}.$$

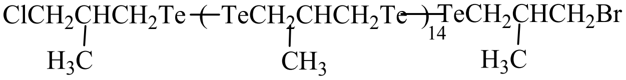
After the addition of dihalogenide **I** to the obtained solution, tellurocol **II** was isolated in 82% yield (calculated on the tellurium taken for the reaction) as a viscous black product. When the temperature of the reaction was 50–55°C, no products of elimination (methylpropene or methylcyclopropane) were detected.



$$n\,\mathrm{BrCH_2\underset{CH_3}{CH}CH_2Cl} \xrightarrow[-n\,\mathrm{KCl};\;-n\,\mathrm{KBr}]{n\,\mathrm{K_2Te_2}} \left(\mathrm{TeCH_2\underset{CH_3}{CH}CH_2Te}\right)_n$$

I **II**

The obtained oligomeric tellurocol contains, according to the elemental analysis data, 2% of the residual halogen. Taking into account that the chlorine and bromine atoms in the macromolecule are terminal, the molecular mass of the oligomer was estimated at ~5000 Da. Regarding the molecular mass of the monomer unit of oligomer **II** as 314 the average formula of compound **III** should be $C_{64}H_{128}Te_{30}ClBr$, which satisfactorily corresponds to the data of elemental analysis.



$$\mathrm{ClCH_2\underset{H_3C}{CH}CH_2Te}\left(\mathrm{TeCH_2\underset{CH_3}{CH}CH_2Te}\right)_{14}\mathrm{TeCH_2\underset{H_3C}{CH}CH_2Br}$$

III

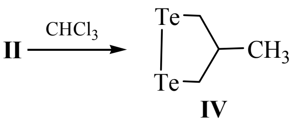
When using other ratios Te:KOH, tellurocols with various length of the telluride fragments in the macromolecule were obtained. Their properties are similar to those of tellurocol **II**. Their molecular mass varies from 2000 to 6000 Da and decreases with the elongation of the polytelluride chain. For example, for Te:KOH = 1.25:1 oligomer **IIa** was obtained, which, according to the data of elemental analysis, contains not only ditelluride, but also tritelluride chains. Taking into account the residual content of the halogens (5.9%), its molecular mass is ~2000 Da.

$$\mathrm{ClCH_2\underset{H_3C}{CH}CH_2Te}\left(\mathrm{TeCH_2\underset{CH_3}{CH}CH_2TeTeTeCH_2\underset{CH_3}{CH}CH_2Te}\right)_2\mathrm{TeCH_2\underset{H_3C}{CH}CH_2Br}$$

IIa

When treated with chloroform, tellurocol **II** forms bright blue solutions, which, from the data of chromatomass-spectrometry and NMR spectroscopy, contain 4-methyl-1,2-ditellurolane **IV**.

Similarly, from the oligomer synthesized by the reaction of 1-bromo-3-chloropropane with tellurium, we have earlier obtained the solutions of 1,2-ditellurolane, which was extremely unstable [12] although could be stabilized in the presence of nitrosodurene [13]. As distinct of that, ditellurolane **IV** unexpectedly turned out to be much more stable: its solutions remained unchanged (according to the UV and NMR spectroscopy) for 3–4 days, and only after that the precipitate appeared, but the solution retained its intense color for several more days.

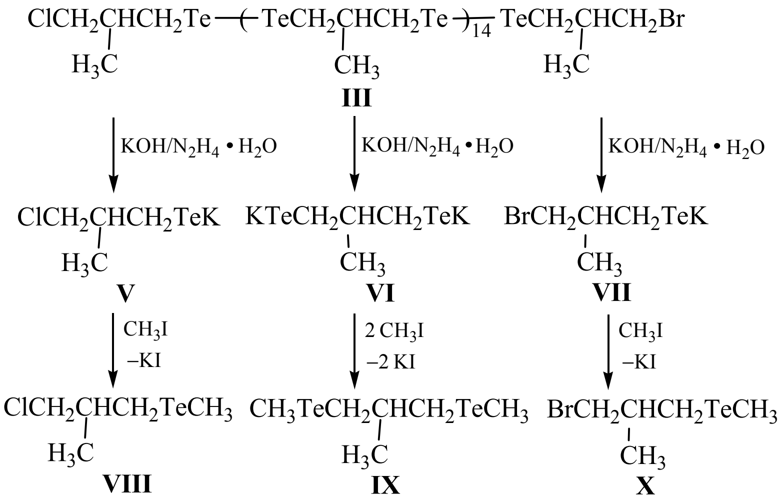


IV

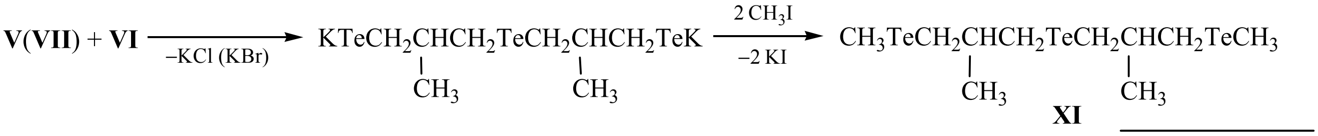
The UV spectrum of oligomer **II** in the absence of solvent (in film) does not contain absorption bands characteristic of ditellurolane **IV**. This suggests that in the reaction of dichloride **I** with K_2Te_2 only oligomer **II** is formed; no cyclic product is formed, apparently, because of high internal strains. The less strained six- and seven-membered rings, for example, from chlorex, are formed rather easily under proper conditions [5].

Similar to other organochalcogen compounds containing dihalogenide fragments Y–Y (Y = S, Se, Te) [2], tellurocol **II**, under the action of the system hydrazine hydrate–KOH suffers the reductive splitting at the Te–Te bonds with the formation of the corresponding tellurolate derivatives **V, VI, VII**, which, without isolation, are readily methylated with methyl iodide. The process of reductive splitting can be schematically represented, using the average formula of compound **III**, as shown further.

2-Methyl-1,3-bis(methyltellanyl)propane **IX** is formed in 48% yield, the monotelluride compound **VIII**, in 3% yield (from GLC, NMR, and chromatomass-spectrometry), whereas compound **X** was detected in trace amounts only by the method of chromatomass-spectrometry. Apart from compounds **VIII–X**, 4,8-dimethyl-2,6,10-tritellurundecane **XI** was identified in the mixture of the products using the methods of chromatomass-spectrometry with chemical ionization and ^{125}Te NMR spectroscopy (yield 21%). The formation of compound **XI** occurs, most probably with the participation of monotelluride derivatives **V** and **VII**.



The use of the methods of chromatomass-spectrometry with chemical ionization for the analysis of the mixture of the products of the reductive splitting of tellurocol **IIa** allowed to identify ditellurolane **IV**, which, apparently, is formed due to partial oxidation of potassium ditellurolate **VI** (yield ~1%).

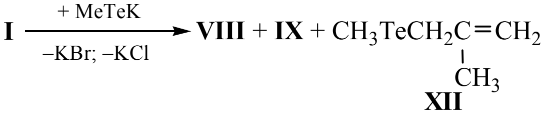


XI

Passing air through the reaction mixture after the reduction of tellurocol **II** does not increase the yield of compound **IV**, perhaps, due to large excess of hydrazine in the reaction mixture.

$$\mathbf{VI} \xrightarrow[-2\,KOH]{0.5\,O_2 + H_2O} \mathbf{IV}$$

Considering the possibility of using compound **IX** as a ligand for preparation of metal complexes [14], we have studied an alternative method for its synthesis based on the preliminary reduction of dimethylditelluride by the system hydrazine hydrate–KOH to potassium methane tellurolate MeTeK and its subsequent reaction with dichloride **I**. However, the maximum yield of product **IX** was 36%. Also the product of partial substitution of the halogen atoms by the methyltellanyl group, 2-methyl-1-methyltellanyl-3-chloropropane **VIII** is formed in 43% yield. Rapid introduction of excess of dihalogenide **I** into the solution of potassium methane tellurolate affords compound **VIII** in 75% yield, the yield of 2-methyl-1,3-bis(methyltellanyl)propane **IX** being as low as 6%. In the course of the reaction, product **VIII** undergoes partial dehydrochlorination with the formation of 2-methyl-3-methyltellanyl-1-propene **XII** (yield 3–10%).



XII

Product **X** was detected by chromatomass-spectrometry in trace amounts only when using the excess of dihalogenide **I**. Probably, it is this product which suffers easy dehydrobromination leading to compound **XII**.

Therefore, based on 1-bromo-2-methyl-3-chloropropane and elemental tellurium in the system hydrazine hydrate–KOH organoelemental oligomers can be synthesized, tellurocols, from which 4-methyl-1,2-ditellurolane and 2-methyl-1,3-bis(methyltellanyl) propane are formed.

The reaction of 1-bromo-2-methyl-3-chloropropane with dimethylditelluride in the used system, apart from 2-methyl-1,3-bis(methyltellanyl)propane, allows obtaining 2-methyl-1-methyltellanyl-3-chloropropane, a promising reagent for the synthesis of functionalized organotellurium compounds. No elimination of halogen from 1-bromo-2-methyl-3-chloropropane was observed in the studied reactions.

EXPERIMENTAL

UV absorption spectra were registered on a UV-Vis Lambda-35 spectrometer for thin films on quartz glass and for solutions in $CHCl_3$ in quartz cells of 0.1 cm thickness. IR spectra were recorded in thin film and in KBr pellets on a Bruker IFS-25 spectrometer. ^1H, ^{13}C, and ^{125}Te NMR spectra were taken on a Bruker DPX 400 spectrometer (400.13, 100.62, and 126.2 MHz, respectively) in $CDCl_3$ solutions, internal standard TMS (^1H, ^{13}C) and Me_2Te (^{125}Te). Electron ionization mass spectra (70 eV) were recorded on a Shimadzu GCMS-QP5050A instrument (quadruple mass analyzer, the range of detected masses was from 34 to 650 Da). The chemical ionization positive ion mass spectra were registered on an Agilent 5975C instrument with methane as a gas-reagent. The samples were introduced via the Agilent 6890N chromatograph.

The reactions were monitored and the formed liquid products were analyzed on a LKhM 80-MD-2 chromatograph (column 2000×3 mm, liquid phase DC-550, 5% on Chromaton N-AW-HMDS, linear temperature programming, 12 deg min^{-1}, carrier gas helium).

Chromatographic separation of the studied compounds was performed on a capillary column SPB–5 (60 m×0.25 mm× 0.25 μm), carrier gas helium, flow rate 0.7 ml min^{-1}, temperature of injector and ion source 250°C, pressure 150 kPa, temperature programming from 60 to 250°C with the rate 10 deg min^{-1}.

Tellurocol II. To the solution of potassium ditelluride prepared from 1.4 g (0.025 mol) of KOH in 10 ml of hydrazine hydrate and 3.19 g (0.025 mol) of powdered tellurium, 2.14 g (0.0125 mol) of 1-bromo-2-methyl-3-chloropropane **I** was added dropwise at 29°C, the mixture was stirred for 1.5 h at 50–55°C. The reaction mixture was cooled, the precipitated polymer was separated, washed with water, with small portions (5 ml) of ethanol and ether, dried in a vacuum. Yield of tellurocol **II** was 3.2 g (82% calculated on the tellurium taken), viscous, sticky mass of black color. *M* 5500. Found, %: C 15.62; H 2.35; Te 79.93; (Cl+Br) 2.02. $C_{64}H_{128}Te_{30}BrCl$. Calculated, %: C 15.73; H 2.60; Te 79.28; (Cl+Br) 2.36. IR spectrum, ν, cm^{-1}: 2952, 2861, 1631, 1450, 1400, 1368, 1313, 1299, 1262, 1172, 1104, 1052, 995, 945, 883, 853, 827, 768, 687, 642, 612. In the UV spectrum of tellurocol **II** the absorption bands at 570 and 650 nm are lacking.

Tellurocol IIa. Under similar conditions from 1.4 g (0.025 mol) of KOH in 10 ml of hydrazine hydrate, 4.0 g (0.03 mol) of powdered tellurium, and 2.14 g (0.0125 mol) of 1-bromo-2-methyl-3-chloropropane **I** 4.0 g (85% to the taken tellurium) tellurocol **IIa** was obtained as viscous, sticky mass of black color. *M* 2000. Found, %: C 13.80; H 2.10; Te 77.90; (Cl+Br) 5.90. $C_{24}H_{48}Te_{12}BrCl$. Calculated, %: C 14.52; H 2.42; Te 77.23; (Cl+Br) 5.83. IR spectrum, ν, cm^{-1}: 2970, 2918, 2861, 1635, 1450, 1370, 1175, 1116, 1034, 883, 714, 604.

4-Methyl-1,2-ditellurolane (IV). Tellurocol **II** was treated with $CDCl_3$, the obtained dark-blue solution, according to the data of chromatomass-spectrometry and ^1H NMR spectroscopy, contained 4-methyl-1,2-ditellurolane **IV**. ^1H NMR spectrum, δ, ppm: 1.06 d (3H, $\underline{Me}CH$, ^3J 6.4 Hz), 3.21 m (2H, CH_2Te, H_A, $^2J_{AB}$ 10.0, ^3J 6.4 Hz), 3.50 d. d (2H, CH_2Te, H_B, ^3J 3.6 Hz), 3.65 d (1H, CH). Mass spectrum (chemical ionization), *m/z* (^{130}Te) (*I*, %): 316 (24) $[M]^{+\bullet}$. In the UV spectrum (solution in $CDCl_3$) absorption bands at 573 and 657 nm are present.

Reductive splitting of tellurocol II and alkylation with methyl iodide. 2-Methyl-1,3-bis(methyl-tellanyl)propane (IX). The mixture of 1.8 g (0.032 mol) KOH in 8 ml of hydrazine hydrate and 2 g (0.006 mol) of oligomer **II** was stirred for 2 h at 80°C, cooled to room temperature, 1.8 g (0.013 mol) of methyl iodide was added dropwise, the mixture was stirred for another 0.5 h at 35°C and after cooling the lower organic layer (1.05 g) was separated and washed with water. From the GC, NMR and chromatomass-spectrometry data, the content of the target 2-methyl-1,3-bis(methyltellan-yl)propane **IX** was 48% calculated on the taken oligomer **II**. The product decomposes when trying to distil it in a vacuum. Found, %: C 20.92; H 3.99; Te 74.55. $C_6H_{14}Te_2$. Calculated, %: C 21.10; H 4.10; Te 74.79. ^1H NMR spectrum, δ, ppm: 1.09 d (3H, CH_3C, ^3J 6.6 Hz), 1.87 m (1H, CH), 1.89 s (CH_3Te, $^2J_{TeH}$ 20 Hz), 2.72 m (4H, CH_2Te, ^2J 12 Hz). ^{13}C NMR spectrum, δ_C, ppm: –21.54 (CH_3Te, $^1J_{CTe}$ 164 Hz), 14.48 (CH_2Te, $^1J_{CTe}$ 161 Hz), 22.87 ($\underline{C}H_3C$), 36.25 ($\underline{C}HCH_3$). ^{125}Te NMR spectrum, δ_{Te}, ppm: 83.6 m ($^2J_{TeH}$ 20 Hz). Mass spectrum of compound **IX**, *m/z* (^{130}Te): 346 $[M]^{+\bullet}$. Beside, the organic layer, according to the GC, NMR and chromatomass-spectrometry data, contains 2-methyl-1-methyl-tellanyl-3-chloropropane **VIII**, 2-methyl-1-methyl-tellanyl-3-bromopropane **X**, 4,8-dimethyl-2,6,10-tri-tellurundecane **XI**. ^1H NMR spectrum of compound **VIII**, δ, ppm: 1.02 d (3H, CH_3C, ^3J 6.7 Hz), 1.83 m (3H, CH_3Te, $^2J_{TeH}$ 10 Hz), 1.92 m (1H, CH), 2.64 m (2H, CH_2Te, ^2J 12.6, ^3J

6.9 Hz), 3.46 m (2H, CH_2Cl, ^2J 10.6, ^3J 5.8 Hz). ^{125}Te NMR spectrum of compound **XI**, δ_{Te}, ppm: 153.9 ($TeCH_3$), 226.1 (CH_2TeCH_2). Mass spectra of compounds **VIII, X, XI**, *m/z* (^{130}Te): $[M]^{+\bullet}$ 236, 282, 532, respectively. The yields of compounds are given in the text.

Reductive splitting of Me_2Te_2 and alkylation of 1-bromo-2-methyl-3-chloropropane (I). 2-Methyl-3-methyltellanyl-1-propene (XII). The mixture of 3.4 g (0.06 mol) of KOH in 15 ml of hydrazine hydrate and 3.5 g (0.012 mol) of Me_2Te_2 were stirred for 2 h at 80° C, cooled to room temperature, 2 g (0.012 mol) of 1-bromo-2-methyl-3-chloropropane **I** was added dropwise, stirred for 2 h at 55–60°C, cooled, the lower organic layer (3.5 g) was separated, which from the GC, NMR, and chromatomass-spectrometry data, contains 2-methyl-1-methyltellanyl-3-chloropropane **VIII**, 2-methyl-1,3-bis(methyltellanyl)propane **IX**, 2-methyl-1-methyltellanyl-3-bromopropane **X**, 2-methyl-3-methyltellanyl-1-propene **XII**. Spectral characteristics of compound **IX** are identical to those given above. Mass spectra of compounds **VIII, X** are given above. Mass spectrum of compound **XII**, *m/z* (^{130}Te): $[M]^{+\bullet}$ 200. The yields of the products are given in the text.

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