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Reaction of 1-Bromo-3-chloropropane with Tellur and Dimethyltelluride in the System of Hydrazine Hydrate–Alkali

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Abstract—A synthesis of oligomeric substance of thiocol type, the poly(trimethyleneditelluride), from 1-bromo-3-chloropropane and elemental tellurium is performed using a hydrazine hydrate–alkali system. Reductive splitting of the tellurocol followed by alkylation with methyl iodide give rise to preparation of bis(methyltelluro)propane, which was synthesized also from dimethyltelluride and 1,3-dihalopropanes using the $N_2H_4 \cdot H_2O$/KOH system. Mass spectra of the synthesized low molecular weight organotellurium compounds are considered.

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Organic compounds of tellurium are highly effective ligands for the complex formation [1–3] and reagents for the synthesis of complicated organic compounds [4, 5]. Polimeric materials containing tellurium attract attention as the compounds for creation of new electronic components [6, 7]. Earlier we by reaction of 1-bromo-3-chloropropane with elemental sulfur [8, 9] and selenium [10] in the system of hydrazine hydrate–base obtained oligomeric substances of thiocol type which were used for the synthesis of various low molecular weight organosulfur and organoselenium compounds.

In this communication we publish our results on the study of behavior of tellurium and some of its derivatives in the reaction with 1-bromo-3-chloropropane in the base-reducing system of hydrazine hydrate–alkali. In such a system tellurium is activated at the ratio Te : KOH = 1 : 1 due to formation of Te_2^{2-} anion [11]:

$$\begin{aligned} &4Te + 4KOH + NH_2NH_2 \cdot H_2O \\ &\longrightarrow 2K_2Te_2 + N_2 + 5H_2O. \end{aligned} \qquad (1)$$

Further reaction of K2Te2 (Te_2^{2-}) with 1-bromo-3-chloropropane leads to formation of a black product.

$$\overset{ClCH_2CH_2CH_2Br}{\xrightarrow[\text{–KCl, –KBr}]{K_2Te_2}} \left(TeCH_2CH_2CH_2Te \right)_n .$$

From the results of elemental analysis we estimated average molecular weight of the oligomer obtained (~3400). Taking into consideration the residual content of halides we propose for this substance structure **I**:

$$ClCH_2CH_2CH_2Te(TeCH_2CH_2CH_2Te)_{10}TeCH_2CH_2CH_2Br.$$

I

The IR spectrum (KBr) of compound **I** is typical of polymeric materials. It contains the following bands: 2956, 2919, 2850, 1435, 1400, 1330, 1248, 1168, 1118, 906, 787, 756, 693, 478 cm^{-1}. The bands 1168 and 693 cm^{-1} are the strongest. Existing data on vibration spectra of organotellurium compounds do not allow their unambiguous assignment.

Like the related thiocols [8, 9] and selenocols [10] the system of hydrazine hydrate–KOH splits oligomer **I** forming a homogenous solution (reductive splitting of Te–Te bonds [12]).

$$\mathbf{I} \xrightarrow{N_2H_4 \cdot H_2O/KOH} KTeCH_2CH_2CH_2TeK. \qquad (2)$$

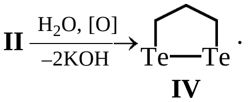
II

Potassium ditellurate **II** without isolation from the solution was methylated with methyl iodide. From the organic layer formed 1,3-bis(methyltelluro)propane (**III**) was isolated in 47.5% yield (on the tellurium taken for the reaction1). Dimethyltellur is formed in 25% yield.

$$\mathbf{II} \xrightarrow[-2KI]{2CH_3I} \underset{\mathbf{III}}{CH_3TeCH_2CH_2CH_2TeCH_3}. \qquad (3)$$

Compound **III** is the most effective ligand among the tellurium containing ones [3], therefore the development of a simple method for its synthesis is independently of practical importance.

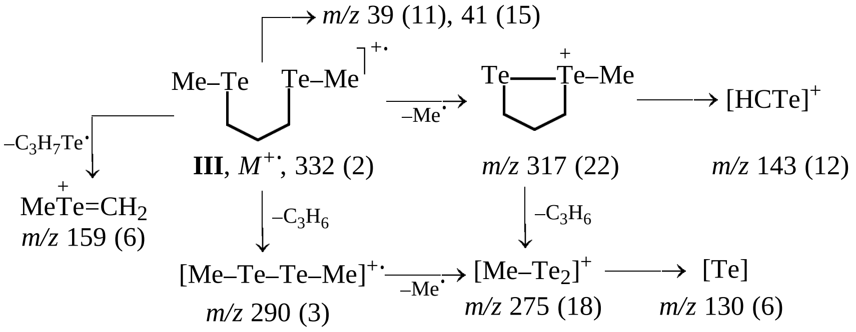
According to the data of chromato-mass spectrometry, the organic layer in reactions 2 and 3 also contains 1,2-ditellurolane (**IV**), *m/z* 302 for ^{130}Te [13], yield 3%. The the latter most probably is formed at the oxidation of ditellurolate **II**.



IV

Structure of 1,3-bis(methyltelluro)propane (**III**) is confirmed by the methods of ^1H NMR spectroscopy and mass-spectrometry. In its ^1H NMR spectrum the protons of CH_3Te group induce a singlet at 1.84 ppm, the CCH_2C protons give a quintet centered at 2.10 ppm, ^3J 7.3 Hz, the CH_2Te protons induce a triplet at 2.65 ppm. Mass-spectrum contains a family of peaks of the molecular ion with the intensity typical for the particles with two Te atoms. The molecular ion **III** fragmentation is the same as in the case of related thio [8] and selenium [10] analogs (Scheme 1, *m/z* of the tellurium-containing ions is given for 130Te, the intensities are scaled to overall ion current).

Scheme 1.



1,3-Bis(methyltelluro)propane (**III**) was also obtained by us in an authentic synthesis in 86% yield from dimethyltelluride and 1,3-dibromopropane according to the following sequence:

$$2Ne_2Te_2 + N_2H_4 \cdot H_2O + 4KOH$$

$$\longrightarrow 4MeTeK + N_2 + 5H_2O, \qquad (4)$$

$$2MeTeK + Br(CH_2)_3Br \xrightarrow[-2KBr]{} \mathbf{III}. \qquad (5)$$

Then 1-bromo-3-chloropropane is involved in the reaction (5) instead of 1,3-dibromopropane, a mixture of two compounds is formed: **III** (yield 17% on the dimethyltelluride taken into reaction) and methyl(3-chloropropyl)telluride (**V**) (44%).

$$MeTeK \xrightarrow{Cl(CH_2)_3Br} \mathbf{III} + \underset{\mathbf{V}}{CH_3TeCH_2CH_2CH_2Cl}. \qquad (6)$$

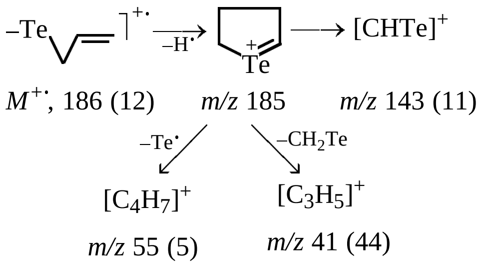
In ^1H NMR spectrum of the mixture of compounds **III** and **V** in addition to the signals of compound **III** occur those of **V**: 1.91 s (CH_3Te), 2.13 quintet (CCH_2C), 2.73 t (CH_2Te), 3.60 t (CH_2Cl), ^3J 7.0 Hz. Mass-spectrum of compound **V** contains a family of peaks of molecular ion with medium intensity, the signal distribution typical of the presence of one tellurium and one chlorine atom in the particle (for ^{130}Te and ^{35}Cl *m/z* 222 $[M]^+$). The most strong fragmental peaks correspond to the ions $[CH_3TeCl]^+$ *m/z* 180, $[CH_3Te]^+$ *m/z* 145, $[CH_2Te]^+$ *m/z* 144, Te^+ *m/z* 130, $[CH_2Cl]^+$ *m/z* 49, and $[C_3H_5]^+$ *m/z* 41.

By the method of chromato-mass spectrometry among the products formed in reaction (5) we also detected methylallyltelluride (**VI**) (yield ~1%). This compound is probably formed through a partial dehydrochlorination of nonsymmetrical telluride **V** in the basic-reductive system.

$$\mathbf{V} \xrightarrow[-KCl,\ -H_2O]{KOH} \underset{\mathbf{VI}}{CH_3TeCH_2CH{=}CH_2}.$$

In the mass-spectrum of telluride **VI** the molecular peak appears as a typical cluster of isotopic peaks ($[M]^{+\cdot}$ 186 *m/z* for ^{130}Te) with intensity ratio characterisitic of the presence of one tellurium atom. Its fragmentation is shown in the Scheme 2.

Scheme 2.



Methylallyltelluride **VI** was prepared in 66.5% yield by authentic route from allyl bromide and dimethyltelluride in a hydrazine hydrate–alkali system. The potassium methyltellurate obtained in reaction (2) was taken into reaction with allyl bromide and only telluride **VI** was obtained.

$$\mathrm{MeTeK + BrCH_2CH{=}CH_2 \xrightarrow[-KBr]{} \textbf{VI}}.$$

Compound **VI** has been described in [14]. It was prepared by reaction of allylmagnesium halides with tellurium in an inert atmosphere at low temperature followed by methylation with methyl iodide (00C). Methylallyltelluride **VI** was isolated in dark in 56% yield. The method of synthesis of telluride **VI** proposed by us is based on the more available reagents and is more useful in technological aspect.

Thus, from 1-bromo-3-chloropropane and tellurium in the system of hydrazine hydrate–KOH can be synthesized tellurocol which enters readily to reductive splitting, and this enables preparation of 1,3-bis(methyltelluro)propane. The latter compound can also be synthesized from dihalopropane and dimethyltelluride.

EXPERIMENTAL

IR spectra were registered on a Specord IR-75 instrument in thin layer and on a Bruker IFS-25 in KBr pellets. ^{1}H and ^{13}C NMR spectra were registered on a Bruker DPX-400 spectrometer (400.1 and 100.6 MHz, respectively) as solvents in $CDCl_3$, internal reference HMDS.

The mass spectra were registered on a chromatomass spectrometer Shimadzu GCMS-QP5050A (SPBTM-5 column, 60000×0.25 mm), stationary phase film 0.25 μm, injector temperature 250°C, carrier gas helium, flow rate 0.7 ml min^{-1}, programmed rise of temperature from 60 to 260°C 15 deg. Temperature of detector 250°C, mass analyzer quadrupole, electron ionization, energy 70 eV, temperature of ion source 200°C, the detectable mass range is 34 to 650 D.

Analysis of the formed liquid compounds was performed on a LKhM 80-MD-2 chromatograph, column 2000×3 mm, liqid phase XE-60 (5%), linear temperature programming 12 deg min^{-1}, carrier gas helium.

Poly(trimethylditelluride) (I). To a solution of 2.8 g of KOH in 20 g of hydrazine hydrate at 75°C was added 6.38 g of tellurium powder for 0.5 h. The dark violet reaction mixture was kept for 2 h at 85°C and cooled to room temperature. Then in 15 min 5.85 g of 1-bromo-3-chloropropane was added till decolorization of the reaction mixture. The mixture was kept for 1.5 h at 60–65°C, cooled, and tellurocol dropped as sticky black mass was separated from aqueous layer, washed repeatedly with cold and hot water, and then dried in a vacuum. Yield 7.2 g (98% on the taken tellurium), mp (decomp.) 55–90°C. Found, %: C 12.45, H 2.05, (Br + Cl) 3.42, Te 81.88. $C_{36}H_{72}Te_{22}BrCl$. Calculated, %: C 12.60, H 2.10, Br + Cl 3.36, Te 81.92.

1,3-Bis(methyltelluro)propane (III). *a.* A mixture of 2.52 g KOH in 11.4 g of hydrazine hydrate and 2.7 of g poly(trimethyleneditelluride) (**I**) was stirred for 1.5 h at 75°C to complete dissolving of the polymer. Mixture was cooled to room temperature and 5.1 g of methyl iodide was added in 0.5 h. Stir was continued for 0.5 h at 40–43°C and after cooling organic layer (bottom) was separated (2.02 g). According to the data of GLC and chromato-mass spectrometry it contained compound **III**, dimethyltelluride and 1,2-ditellurolane **IV**. Yield of compound **III** is 47.5%.

b. To a solution of 1.17 g of KOH in 5 g hydrazine hydrate 1.2 g of dimethyltelluride was added. The mixture was heated with stirring for 1 h at 75-80°C, then cooled to 30°C and for 15 min 1.7 g of 1,3-dibromopropane was added to it. The reaction mixture was heated for 0.5 h at 60–62°C and after cooling the bottom (organic) layer (1.0 g) was separated. According to GLC and ^{1}H NMR data it consisted purely of 1,3-bis(methyltelluro)propane **III**, yield 80%.

c. To a solution of 3.5 g of dimethyltelluride in the system of hydrazine hydrate (15 ml)–KOH (3.4 g) obtained in the *b* procedure was added at 50°C 3.8 g of 1-bromo-3-chloropropane. The mixture was stirred for 1 h at 50–60°C, then cooled and organic layer

(3.2 g) was separated. The data of GLC, chromato-mass spectrometry and ^{1}H NMR spectroscopy indicated the presence of compound **III**, methyl(3-chloropropyl)telluride (**V**) and methylallyltelluride (**VI**) (yields were shown in the main part of the communication).

Methylallyltelluride (VI). To a solution of 3.6 g of KOH in 16 g of hydrazine hydrate 3.62 g of dimethyltelluride was added and the mixture was stirred for 2 h at 80–85°C to complete dissolving of dimethyltelluride. After cooling to 25°C, 3.05 g of allyl bromide was added in 20 min, then stir was continued for 1 h at room temperature and the bottom (organic) layer (3.1 g) was separated. Compound **VI** was isolated by distillation in a vacuum: bp 56°C (30 mm Hg) (published: 41°C at 13 mm Hg) [14]). Found, %: C 26.03, H 4.41, Te 68.74. C_4H_8Te. Calculated, %: C 26.14, H 4.36, Te 69.50. IR spectrum, cm^{-1}: 3077, 3029, 3000, 2972, 2921, 2849, 1624, 1426, 1398, 1291, 1219, 1190, 1128, 1042, 984, 901, 849, 676, 524, 491. ^{1}H NMR spectrum, δ, ppm: 1.86 s (CH_3Te), 3.31 d (CH_2Te), 4.80 m (CH_2=), 5.94 m (CH=). ^{13}C NMR spectrum, δ_C, ppm: (–20.70) (CH_3Te), 5.31 (CH_2Te), 114.24 (CH_2=), 136.02 (CH=).

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