

# Reaction of 1,1-Dichloroethane with Tellurium in the System Hydrazine Hydrate–Potassium Hydroxide

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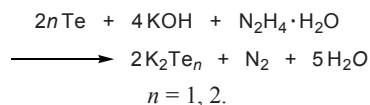
**Abstract**—The reaction of 1,1-dichloroethane with tellurium in the system hydrazine hydrate–potassium hydroxide gave ethyltellanyl derivatives as a result of replacement of one chlorine atom in the substrate by tellurium, and of the other, by hydrogen. Probable mechanisms of reduction of the C–Cl bond and mass spectra of the products were considered. The mass spectra of ditelluroacetals revealed unusual rearrangement of the molecular ion, leading to the formation of Te–Te and new C–C bond.

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Reactions of tellurium with difunctional electrophiles in the presence of reducing agents make it possible to obtain tellurium-containing polymeric products, which may be used in the preparation of new materials for electrotechnics and intermediate products for the synthesis of multidentate tellurium-containing ligands [1, 2].

In the present article we report on the results of our study on unusual behavior of a geminal dihalogen derivative, 1,1-dichloroethane, in the reaction with tellurium and dimethyl ditellurides in the basic reducing system hydrazine hydrate–potassium hydroxide. It is known that this system generates tellurium-containing anions from tellurium and dimethyl ditelluride [3] (Schemes 1, 2).

## Scheme 1.



## Scheme 2.



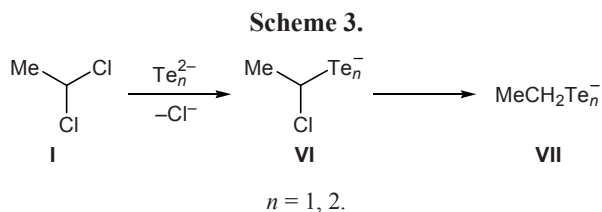
The value of  $n$  in  $\text{Te}_n^{2-}$  depends on the KOH–Te ratio [3]. Equimolar amounts of KOH and Te give rise to predominant formation of potassium ditelluride ( $n = 2$ ), while selective formation of monotelluride

requires a large excess of alkali [KOH–Te ratio should be equal to (6–8):1].

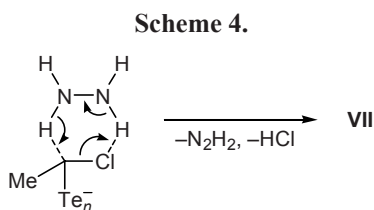
Telluride solutions thus obtained were brought into reaction with 1,1-dichloroethane (**I**). However, we observed no formation of polymeric products with the use of  $\text{K}_2\text{Te}$  or  $\text{K}_2\text{Te}_2$  solution. The reaction mixture retained its intense color even upon addition of excess dichloride **I**. When tellurium was activated with excess alkali (generation of  $\text{K}_2\text{Te}$ ), we isolated by extraction two products: diethyl telluride  $\text{Et}_2\text{Te}$  (yield 8%, calculated on the reacted tellurium) and diethyl ditelluride  $\text{Et}_2\text{Te}_2$  (64%). After separation of organic products, the mixture was treated with hydrochloric acid to recover unreacted tellurium. The conversion of tellurium was 92%. Addition of excess 1,1-dichloroethane (**I**) to the reaction system containing equimolar amounts of KOH and tellurium (generation of  $\text{K}_2\text{Te}_2$ ) resulted in liberation of elemental tellurium even during the process. By extraction we isolated  $\text{Et}_2\text{Te}_2$  in 48% yield (calculated on the reacted tellurium). When the reaction mixture obtained after addition of a required amount of compound **I** (Te–**I** ratio 1:1) was treated with methyl iodide (before decoloration of the hydrazine layer), the following products were formed (according to the GLC, GC–MS, and NMR data):  $\text{Et}_2\text{Te}_2$  (yield 41%, calculated on the reacted tellurium),  $\text{Me}_2\text{Te}_2$  (14%),  $\text{MeTeEt}$  (12%),  $\text{Me}_2\text{Te}$  (1%), and  $\text{Et}_2\text{Te}$  (1%). In addition, we identified methyl 1-chloroethyl telluride (**II**, 4%), ethyl 1-chloroethyl telluride (**III**, 5%), 1,1-bis-

(methyltellanyl)ethane (**IV**), 1-methyltellanyl-1-ethyltellanylethane (**V**), and methyl ethyl ditelluride  $\text{MeTe}_2\text{Et}$ , the yield of each of the three latter compounds being about ~1%

The formation of ethyltellanyl derivatives  $\text{Et}_2\text{Te}$ ,  $\text{MeTeEt}$ ,  $\text{Et}_2\text{Te}_2$ ,  $\text{MeTe}_2\text{Et}$ , and compounds **III** and **V** in the above reactions was surprising. Presumably, generation of the  $\text{EtTe}$  fragment is preceded by replacement of one chlorine atom in molecule **I** by tellurium (Scheme 3).

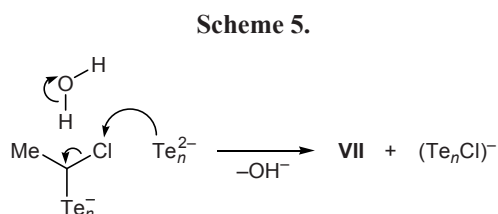


The transformation of anion **VI** into anion **VII** involves reductive replacement of chlorine by hydrogen. Such replacement is known to occur by the action of various reducing agents [4]. Two kinds of reducing agents are present in the systems under study. These are hydrazine and telluride anions. Hydrazine is oxidized to extremely unstable diimide  $\text{HN}=\text{NH}$  [5] which is also capable of acting as effective reducing agent (Scheme 4).



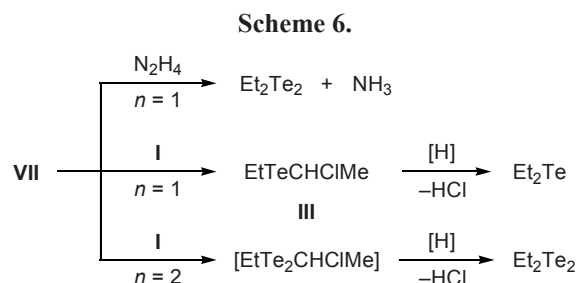
By special experiment we showed that dichloride **I** does not react with hydrazine hydrate–KOH in the absence of tellurium. Compound **I** also remains unchanged in the system  $\text{S}-\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}-\text{KOH}$ .

Tellurium-containing anions are also strong reducing agents, and this property is often responsible for their unusual reactions with electrophiles [6]. According to [6], the reductive action of telluride anions

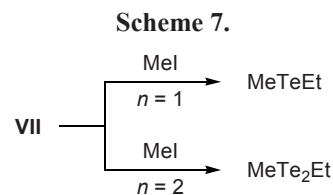


may be represented as halophilic attack, as shown in Scheme 5.

Although species **VI** is anionic, the possibility for halophilic attack by  $\text{Te}_n^{2-}$  ion is determined by high polarizability of tellurium-containing anions. The subsequent transformation of  $[\text{Te}_n\text{Cl}]^-$  ion leads to liberation of elemental tellurium [7]. The fact that the major product in the reaction of dichloride **I** with tellurium activated to  $\text{K}_2\text{Te}$  is diethyl ditelluride implies that participation of telluride ions in the reduction process is more likely to follow Scheme 3. Diethyl ditelluride is formed as a result of further transformations of anion **VII** (Scheme 6).

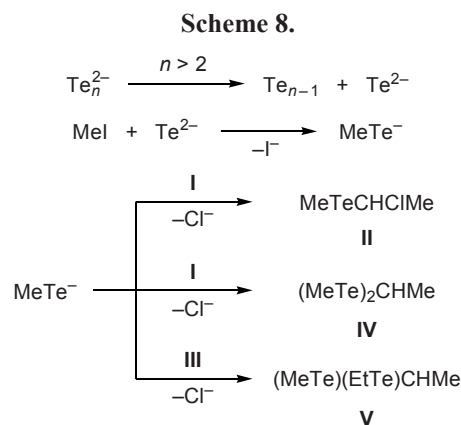


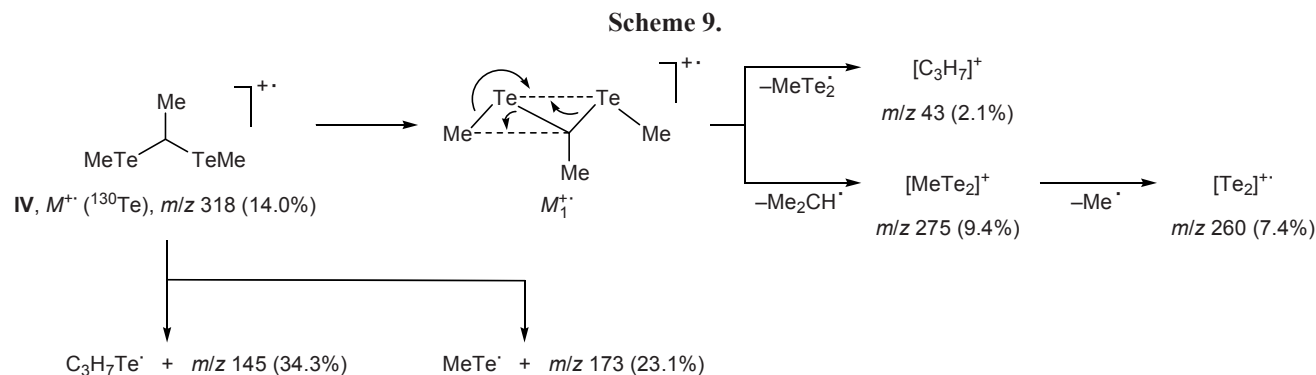
When  $\text{MeI}$  is added to the reaction mixture, methyltellanyl derivatives are obtained (Scheme 7).



The formation of compounds **II**, **IV**, and **V** suggests participation of  $\text{MeTe}^-$  anion which can be generated from methyl iodide and  $\text{Te}^{2-}$  (Scheme 8).

Thus the main pathway in the reaction of 1,1-dichloroethane (**I**) with tellurium in the system hydrazine





hydrate-KOH is that leading to ethyltellanyl derivatives as a result of nucleophilic replacement of one chlorine atom in molecule **I** by tellurium and reductive replacement of the other chlorine atom by hydrogen.

The reaction of dichloride **I** with dimethyl ditelluride activated according to Scheme 2 gave the following products:  $\text{Me}_2\text{Te}$  (8%),  $\text{MeTeEt}$  (5%), 1,1-bis-(methyltellanyl)ethane (**IV**, 27%), and  $\text{MeTe}_2\text{Et}$  (36%). Also, traces of **V** were detected, and 12% of initial  $\text{Me}_2\text{Te}_2$  was recovered from the reaction mixture. The above products are likely to be formed according to the schemes proposed for the reaction with tellurium with participation of  $\text{MeTe}^-$ ,  $\text{Te}_2^{2-}$ ,  $\text{Te}^{2-}$ , and  $\text{EtTe}^-$  anions. We can state that ethyltellanyl derivatives are also formed in the reaction of 1,1-dichloroethane (**I**) with dimethyl ditelluride in the system  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ -KOH.

Mono- and ditelluride derivatives  $\text{Me}_2\text{Te}$ ,  $\text{Me}_2\text{Te}_2$ ,  $\text{MeTeEt}$ ,  $\text{MeTe}_2\text{Et}$ , and  $\text{Et}_2\text{Te}_2$  were identified by GLC, GC-MS, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR using authentic samples [9, 10]. The other compounds were identified by GC-MS and  $^1\text{H}$  NMR. All the examined compounds containing a methyltellanyl group characteristically displayed in the mass spectra  $[\text{MeTe}]^+$  ion peak cluster ( $m/z$  145 for  $^{130}\text{Te}$ ) with the intensity ratio corresponding to natural distribution of tellurium isotopes. The mass spectra of ethyltellanyl derivatives contained ion peak clusters with  $m/z$  159 for  $^{130}\text{Te}$ . If both  $\text{MeTe}$  and  $\text{EtTe}$  groups were present, we observed both kinds of ion peak clusters in the mass spectra.

Analysis of the mass spectra of telluroacetals **IV** and **V** revealed an unusual fragmentation path of the

molecular ion, which gave rise to ions  $[M - 43]^+$  ( $m/z$  275) and  $[M - 57]^+$  ( $m/z$  289) together with  $[\text{C}_3\text{H}_7]^+$  ( $m/z$  43) and  $[\text{C}_4\text{H}_9]^+$  ( $m/z$  57), respectively. The formation of these ions may be rationalized by isomerization of the molecular ion to  $M_1^+$  via formation of  $\text{Te}-\text{Te}$  bond, as shown in Scheme 9 for compound **IV**. Analogous rearrangement of the molecular ion of **V** can take two pathways (Scheme 10).

The rearrangement is likely to be initiated by localization of positive charge in the molecular ion on the tellurium atom. Strong electron-donating properties of tellurium atom favor charge delocalization over the neighboring tellurium atom (transition state  $M_1^+$ ), finally leading to the observed fragmentation pattern.

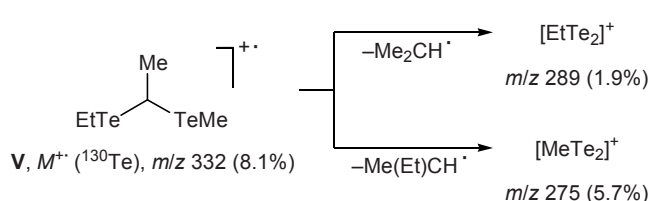
Compound **IV** is isomeric to diethyl ditelluride. However, these compounds are characterized by different retention times and (what is more important) by different fragmentation patterns under electron impact.

Thus the reaction of 1,1-dichloroethane with tellurium in the system hydrazine hydrate-potassium hydroxide involves nucleophilic substitution of one chlorine atom in the substrate by tellurium and reductive replacement of the second chlorine atom by hydrogen. Unexpected reaction products are diethyl ditelluride and other ethyltellanyl derivatives.

## EXPERIMENTAL

The reaction mixtures and products were analyzed by GLC on an LKhM 80-MD-2 chromatograph equipped with a  $2000 \times 3$ -mm column (stationary phase 5% of DC-550 on Chromaton N-AW-HMDS; carrier gas helium; linear oven temperature programming at a rate of 12 deg/min). The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{125}\text{Te}$  NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.1, 100.6, and 126.2 MHz, respectively, using  $\text{CDCl}_3$  as solvent and hexamethyldisiloxane as internal reference.

**Scheme 10.**



The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS-QP5050A instrument (quadrupole mass analyzer, a.m.u. range 34–650). Chromatographic separation was performed using an SPB-5 capillary column, 60 m×0.25 mm×0.25 μm (carrier gas helium, flow rate 0.7 ml/min, inlet pressure 150 kPa; injector and ion source temperature 250°C, oven temperature programming from 60 to 250°C at a rate of 10 deg/min). The  $m/z$  values for tellurium- and chlorine-containing ions are given for  $^{130}\text{Te}$  and  $^{35}\text{Cl}$  isotopes.

**Diethyl ditelluride.** *a.* A solution of 35.0 g (625 mmol) of potassium hydroxide in 110 ml of hydrazine hydrate was heated to 80–85°C, 10 g (78.4 mmol) of powdered tellurium was added in portions under stirring, the mixture was stirred for 3 h at 80–85°C and cooled, 29.1 g (294 mmol) of 1,1-dichloroethane (**I**) was added dropwise, and the mixture was stirred for 9 h at 30–35°C, cooled to 25°C, and extracted with methylene chloride. The extract was dried over  $\text{MgSO}_4$  and evaporated. The residue, 5.1 g, contained (according to the GLC data) 3.7 g of diethyl ditelluride and 1.1 g of diethyl telluride. The aqueous hydrazine layer (after extraction) was poured into a mixture of ice with 180 ml of hydrochloric acid, and the mixture was left to stand for precipitation of tellurium. The mixture was extracted with methylene chloride, the organic phase was separated and dried over  $\text{MgSO}_4$ , and 0.8 g of tellurium (conversion 92%) was filtered off from the aqueous phase. The extract was evaporated to obtain 3.7 g of a residue which contained (GLC) 3.5 g of diethyl ditelluride. Diethyl ditelluride was isolated by distillation of the combined residues under reduced pressure, bp 85°C (1 mm). Mass spectrum,  $m/z$  ( $I$ , % of the total ion current): 318  $[M]^+$  (28.3), 289  $[\text{EtTe}_2]^+$  (27.6), 260  $[\text{Te}_2]^+$  (31.0), 159  $[\text{EtTe}]^+$  (3.9), 130  $[\text{Te}]^+$  (9.2).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.61 t ( $\text{CH}_3$ ), 3.04 q ( $\text{CH}_2$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: -4.43 ( $\text{CH}_2$ ) ( $J_{\text{C,Te}} = 163$  Hz), 19.69 ( $\text{CH}_3$ ).  $^{125}\text{Te}$  NMR spectrum:  $\delta_{\text{Te}}$  160.93 ppm. Diethyl telluride was identified in the extract by GLC and GC–MS data.

*b.* A solution of 3.51 g (62.7 mmol) of potassium hydroxide in 25 ml of hydrazine hydrate was heated to 80–85°C, 8 g (62.7 mmol) of powdered tellurium was added in portions, the mixture was stirred for 3 h at 80–85°C and cooled, 6.21 g (62.7 mmol) of 1,1-dichloroethane (**I**) was added dropwise, and the mixture was stirred for 3 h at 30–35°C. The mixture was cooled and filtered from liberated tellurium (4.7 g), the

filtrate was extracted with methylene chloride, and the extract was dried over  $\text{MgSO}_4$ . An additional amount of tellurium (0.52 g) separated from the aqueous hydrazine layer on storage. The solvent was removed from the extract to obtain 1.7 g of a residue containing 1.64 g of diethyl ditelluride (according to the GLC and GC–MS data).

*c.* A solution of 1.4 g (25 mmol) of potassium hydroxide in 10 ml of hydrazine hydrate was heated to 80–85°C, 3.19 g (25 mmol) of powdered tellurium was added in portions, the mixture was stirred for 3 h at 80–85°C and cooled, 6.21 g (25 mmol) of dichloride **I** was added dropwise, the mixture was stirred for 3 h at 40–45°C and cooled to 25°C, and 7.1 g (50 mmol) of methyl iodide was added. The aqueous hydrazine layer turned colorless, and elemental tellurium separated (2.53 g, conversion 20%). The filtrate was extracted with methylene chloride, and the extract was dried over  $\text{MgSO}_4$  and evaporated. According to the GC and GC–MS data, the residue, 0.76 g, contained  $\text{Me}_2\text{Te}$ ,  $\text{MeTeEt}$ ,  $\text{Et}_2\text{Te}$ ,  $\text{Me}_2\text{Te}_2$ , and  $\text{Et}_2\text{Te}_2$  (the yields were given above in text), which were identical to authentic samples. In addition, the following compounds were identified by GC–MS,  $m/z$  ( $I$ , % of the total ion current): methyl 1-chloroethyl telluride (**II**): 208  $[M]^+$  (15.9), 193  $[M - \text{Me}]^+$  (1.5), 173  $[M - \text{Cl}]^+$  (1.8), 165  $[\text{TeCl}]^+$  (13.2), 145  $[\text{MeTe}]^+$  (37.4), 144  $[\text{CH}_2\text{Te}]^+$ , 130  $[\text{Te}]^+$  (13.6), 63  $[\text{C}_2\text{H}_4\text{Cl}]^+$  (16.7); ethyl 1-chloroethyl telluride (**III**): 222  $[M]^+$  (15.4), 193  $[M - \text{Et}]^+$  (8.6), 159  $[\text{EtTe}]^+$ , 158  $[\text{C}_2\text{H}_4\text{Te}]^+$  (28.5), 130  $[\text{Te}]^+$  (27.7), 63  $[\text{C}_2\text{H}_4\text{Cl}]^+$  (19.8); 1,1-bis(methyltellanyl)ethane (**IV**): 318  $[M]^+$  (14.0), 275  $[\text{MeTe}_2]^+$  (9.4), 260  $[\text{Te}_2]^+$  (7.4), 173  $[M - \text{MeTe}]^+$  (23.1), 145  $[\text{MeTe}]^+$  (34.3), 130  $[\text{Te}]^+$  (9.7), 43  $[\text{C}_3\text{H}_7]^+$  (2.1); 1-ethyltellanyl-1-methyltellanyl ethane (**V**): 332  $[M]^+$  (8.1), 302  $[M - \text{Me}]^+$  (0.9), 289  $[\text{EtTe}_2]^+$  (1.9), 275  $[\text{MeTe}_2]^+$  (5.7), 260  $[\text{Te}_2]^+$  (8.4), 187  $[M - \text{MeTe}]^+$  (13.8), 173  $[M - \text{EtTe}]^+$  (8.0), 159  $[\text{EtTe}]^+$  (16.0), 145  $[\text{MeTe}]^+$  (14.1), 130  $[\text{Te}]^+$  (14.5), 57  $[\text{C}_4\text{H}_9]^+$  (4.8), 43  $[\text{C}_3\text{H}_7]^+$  (3.0); methyl ethyl ditelluride: 304  $[M]^+$  (19.9), 289  $[M - \text{Me}]^+$  (8.7), 275  $[M - \text{Et}]^+$  (9.6), 260  $[\text{Te}_2]^+$  (4.4), 159  $[\text{EtTe}]^+$  (23.2), 144  $[\text{CH}_2\text{Te}]^+$ , 145  $[\text{MeTe}]^+$  (19.6), 130  $[\text{Te}]^+$  (14.6).

**Reaction of 1,1-dichloroethane with hydrazine hydrate–potassium hydroxide.** Compound **I**, 5.0 g (50 mmol), was added dropwise at 25°C to a solution of 2.8 g (50 mmol) of potassium hydroxide in 15 ml of hydrazine hydrate. The mixture was stirred for 3 h at 40–45°C, and unreacted 1,1-dichloroethane (**I**) was separated as organic layer. Likewise, the reaction of **I** with the system  $\text{S}-\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}-\text{KOH}$  was performed. In

this case, 1.6 g (5.0 mmol) of powdered sulfur was added to a solution of KOH in hydrazine hydrate. The mixture was stirred for 6 h at 40–45°C, and unchanged compound **I** was separated.

**Reaction of dimethyl ditelluride with 1,1-dichloroethane (I).** Dimethyl ditelluride, 1.98 g (6.9 mmol), was added to a solution of 1.93 g (34.5 mmol) of potassium hydroxide in 9 ml of hydrazine hydrate, the mixture was stirred for 2.5 h at 80–85°C and cooled to room temperature, 0.68 g (3.4 mmol) of 1,1-dichloroethane (**I**) was added, and the mixture was stirred for 3 h at 30–35°C. After cooling, the organic layer (0.56 g, dark red transparent liquid) was separated, the aqueous hydrazine layer was extracted with methylene chloride, the extract was dried over MgSO<sub>4</sub> and evaporated, and the residue, 1.01 g, was combined with the organic layer and analyzed. The following compounds were identified by GLC and GC–MS: dimethyl telluride, methyl ethyl telluride, 1,1-bis(methyltellanyl)ethane (**IV**), methyl ethyl ditelluride, 1-ethyltellanyl-1-methyltellanyl-ethane (**V**), and unreacted dimethyl ditelluride (for yields, see text). The mass spectra of compounds **IV** and **V** and methyl ethyl ditelluride are given above.

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