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LETTERS TO THE EDITOR

Stereoselective Synthesis of *Z*-2-Bromo-2-phenylvinyltellurium Tribromide and *Z*,*Z*-Bis(2-bromo-2-phenylvinyl)ditelluride

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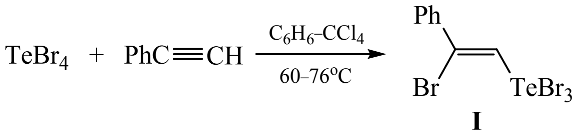
Organotellurium compounds containing vinyl group [1–4] are important intermediates and synthons for organic synthesis. They can be prepared by addition of alkynes to tellurium tetrahalides [5–14].

Reactions of alkynes with tellurium tetrachloride have been reported [1, 5–11]. However, there are a few published data on reactions of tellurium tetrabromide with acetylenes [12–14]. We have developed efficient procedures for the stereoselective synthesis of *E*,*E*-bis-(2-bromovinyl)tellurium dibromide and *E*-(2-bromovinyl)tellurium tribromide by reaction of tellurium tetrabromide with acetylene [12, 13]. The addition of $TeBr_4$ to phenylacetylene and hept-1-yne under reflux gives rise to bis-adducts, bis(2-bromo-2-phenylvinyl)tellurium dibromide and bis(2-bromohept-1-en-1-yl)tellurium dibromide in 89 and 70% yield, respectively, as mixtures of *Z* and *E* isomers with *Z*-isomers pre-vailing (in the case of phenylacetylene *Z* : *E* = 4.5 : 1) [14]. The data on stereoselective synthesis of monoadduct, 2-bromo-2-phenylvinyltellurium tribromide, are absent.

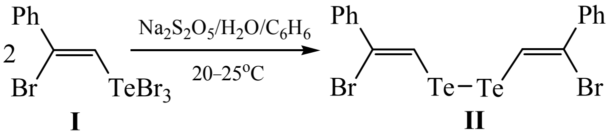
Aiming to synthesize *Z*-2-bromo-2-phenylvinyltellurium tribromide **I**, we investigated the reaction of phenylacetylene with tellurium tetrabromide at equimolar ratio of reactants. Use of a mixture of CCl_4 and benzene allows to stop the process at the stage of monoadduct **I** formation and to carry out the stereoselective reaction. Thus, the heating of the reaction mixture in a mixture of benzene–CCl_4 (1 : 1) at 60–76°C leads to the formation of **I** in a yield of 95% with complete conversion of $TeBr_4$ (Scheme 1).

Scheme 1.



The reduction of compound **I** in a system $Na_2S_2O_5$–H_2O–C_6H_6 results in the previously unknown *Z*,*Z*-bis-(2-bromo-2-phenylvinyl)ditelluride **II** in a yield of 90% (Scheme 2).

Scheme 2.



The structure and composition of compounds **I** and **II** were proved by ^1H, ^{13}C NMR spectroscopy and elemental analysis data. The value of the spin-spin coupling constant between tellurium and the carbon atom having the proton for compounds **I** and **II** equals 219 and 334 Hz, respectively, which corresponds to the direct coupling constants ($^1J_{CTe}$). This indicates the addition of the tellurium atom to the terminal carbon atom of the triple bond of phenylacetylene. The configuration of compounds **I** and **II** was proved by NOESY method.

It is known that organotellurium trihalides and diorganylditellurides are important intermediates in the synthesis of various organotellurium compounds [1, 15]. Organotellurium trihalides and diorganylditellurides were easily reduced to organyltellurolate-anions, which enter into nucleophilic substitution and addition that allows to obtain unsymmetrical tellurides [1, 15]. Organotellurium trihalides add to unsaturated compounds to form unsymmetrical telluranes [15].

In the literature, there is only one paper [13] describing the synthesis of vinyltellurium tribromides and no data exist on the synthesis of bis(2-bromovinyl)-ditelluride. The reaction of tellurium tetrabromide with acetylene proceeds stereoselectively as anti-addition to form *E*-2-bromovinyltellurium tribromide [13].

We studied the addition reaction of tellurium tetrabromide to phenylacetylene, the first example of the stereoselective synthesis of *Z*-2-bromo-vinyltellurium tribromide **I**. Compound **II** is the first representative of 2-bromovinyl ditelluride.

To conclude, we have developed effective procedures for the stereoselective synthesis of previously unknown compounds **I** and **II**, which are promising intermediates for the synthesis of unsaturated organotellurium compounds. Whereas the addition of tellurium tetrabromide to acetylene results in *E*-2-bromovinyltellurium tribromide [13], the reaction with phenylacetylene proceeds as stereoselective *syn*-addition to form the product *Z*-**I**.

***Z*-2-Bromo-2-phenylvinyltellurium tribromide (I).** Yellowish powder, mp 159–162°C (decomp.). ^{1}H NMR spectrun, δ, ppm: 7.53–7.57 m (3H, Ph), 7.72–7.76 m (2H, Ph), 9.56 s (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 125.95 d (=CH, $^1J_{CTe}$ 219 Hz), 127.83 (Ph), 129.21 (Ph), 131.53 (Ph), 135.47 (Ph), 138.23 (BrC=). ^{125}Te NMR spectrum: δ_{Te} 747 ppm. Found, %: C 17.00; H 1.03; Br 58.78; Te 23.00. $C_8H_6Br_4Te$. Calculated, %: C 17.49; H 1.10; Br 58.18; Te 23.23.

***Z*,*Z*-Bis(2-bromo-2-phenylvinyl)ditelluride (II).** Dark red oily substance. ^{1}H NMR spectrum, δ, ppm: 7.21–7.25 m (3H, Ph), 7.45–7.49 m (2H, Ph), 8.21 s (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 108.31 (=CH, $^1J_{CTe}$ 334 Hz), 127.09 (Ph), 127.98 (Ph), 128.39 (Ph), 133.34 (BrC=), 138.10 (Ph). ^{125}Te NMR spectrum: δ_{Te} 365 ppm. Found, %: C 31.08; H 1.90; Br 25.42; Te 41.44. $C_{16}H_{12}Br_2Te_2$. Calculated, %: C 31.03; H 1.95; Br 25.81; Te 41.21.

NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 400.13 (^{1}H), 100.61 (^{13}C), 126.24 MHz (^{125}Te) using DMSO-d_6 (**I**) or $CDCl_3$ (**II**) as solvent.

Structure of the obtained compounds was studied in the Baikal Analytical Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences.

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