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SHORT COMMUNICATIONS

Stereoselective Synthesis of (*Z*,*E*)-Bis(2-chloroethenyl)tellanes

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Abstract—A procedure for the stereoselective synthesis of dichloro[(*Z*)-2-chloro-2-phenylethenyl][(4*E*)-5-chlorooct-4-en-4-yl]-λ^4-tellane and [(*Z*)-2-chloro-2-phenylethenyl][(4*E*)-5-chlorooct-4-en-4-yl]tellane has been developed on the basis of *anti*-addition of tellurium tetrachloride–phenylacetylene monoadduct to oct-4-yne.

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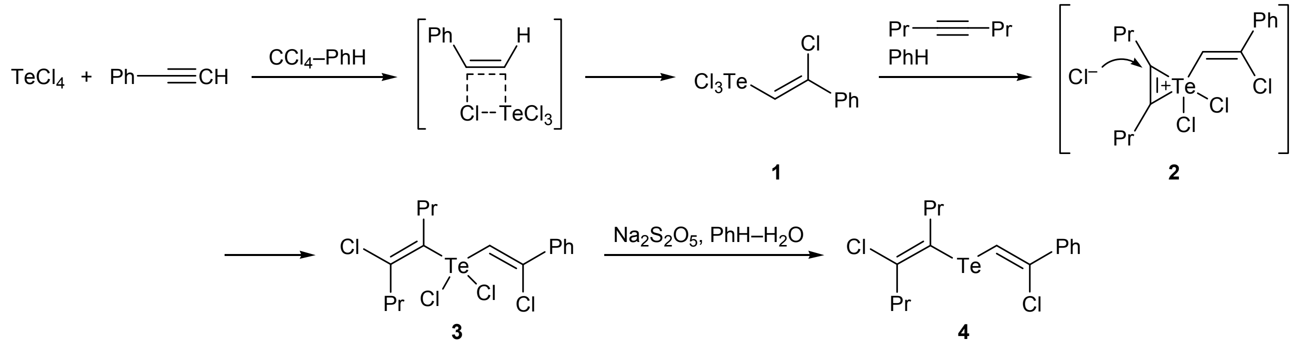
Vinyl tellurides containing a halogen atom at the double bond with a predetermined configuration are important intermediate products in organic synthesis [1]. In particular, they are used for stereoselective synthesis of alkenes via successive substitution of the halogen atom and tellurium-containing group at the double bond in cross-coupling reactions with retention of the double bond configuration [1, 2].

Development of procedures for stereoselective synthesis of 2-halovinyl tellurides is an important problem of organotellurium chemistry. These compounds can be obtained by addition of tellurium tetrachloride to acetylenic compounds, which is often characterized by high regio- and stereoselectivity [1–14]. Tellurium tetrachloride reacts with phenylacetylene [3, 4], phenyl(alkyl)acetylenes [5], and diphenylacetylene [3], as well as with alkylacetylenes and their derivatives [6–9], to give the corresponding *syn*-addition products with *Z* configuration of the double bond. The reactions of tellurium tetrachloride with unsubstituted acetylene [10, 11], hex-3-yne [12], oct-4-yne [13], and phenyl propargyl ether [14] were reported to produce *E* isomers as a result of *anti*-addition.

In this communication we describe the synthesis of the first representatives of bis(2-haloethenyl)-λ^4-tellanes and -λ^2-tellanes having *Z*,*E*-configuration of the double bonds. The reaction of tellurium tetrachloride with phenylacetylene in CCl_4–PhH (9 : 1) followed the *syn*-addition path, presumably through four-membered cyclic transition state, with quantitative formation of trichloro[(*Z*)-2-chloro-2-phenylethenyl]-λ^4-tellane (**1**) [4]. The subsequent stereoselective reaction of **1** with oct-4-yne (*anti*-addition) afforded dichloro[(4*E*)-5-chlorooct-4-en-4-yl][(*Z*)-2-chloro-2-phenylethenyl]-λ^4-tellane (**3**) in 92% yield.

Tellane **1** reacted with oct-4-yne on heating in boiling benzene. The *anti*-addition of **1** to oct-4-yne is likely to proceed through three-membered tellurirenium intermediate **2**, by analogy with the reaction of tellurium tetrachloride with oct-4-yne [13]. The formation of such intermediates was presumed in a number of addition reactions of tellurium-containing electro-



philes with alkynes [3, 12–15]; and in some cases they were isolated and characterized [15].

By reduction of tellane **3** with sodium metabisulfite ($Na_2S_2O_5$) in a two-phase system (water–benzene) we obtained 94% of [(*Z*)-2-chloro-2-phenylethenyl]-[(4*E*)-5-chlorooct-4-en-4-yl]tellane (**4**). The synthesis of **4** can be accomplished in a one-pot manner without isolation of λ^4-tellane **3**. In this case, an aqueous solution of $Na_2S_2O_5$ was added to the benzene solution containing compound **3**, and the mixture was stirred for 2 h at room temperature.

The structure of compounds **3** and **4** was proved by ^1H and ^{13}C NMR spectra and elemental analyses; the configuration of the double bonds therein was determined by NOESY experiments. Compounds **3** and **4** are the first representatives of (*Z*,*E*)-bis(2-haloethenyl)tellanes that are promising intermediate products for organic synthesis.

Dichloro[(4*E*)-5-chlorooct-4-en-4-yl]-[(*Z*)-2-chloro-2-phenylethenyl]-λ^4-tellane (3). A solution of 0.204 g (2 mmol) of phenylacetylene in 4 mL of benzene was added to a mixture of 0.539 g (2 mmol) of tellurium tetrachloride and 36 mL of carbon tetrachloride. The mixture was refluxed for 10 h with stirring under argon, the solvent was removed on a rotary evaporator, and the residue was dried under reduced pressure. We thus isolated 0.743 g (quantitative yield) of tellane **1** as an off-white material. Compound **1**, 0.743 g (2 mmol), was mixed with 20 mL of benzene, a solution of 0.25 g (2.27 mmol) of oct-4-yne in 5 mL of benzene was added, and the mixture was refluxed for 10 h with stirring. The mixture was filtered, the solvent was distilled off on a rotary evaporator, and the residue was dried under reduced pressure. Yield 0.886 g (92%), off-white material. ^1H NMR spectrum, δ, ppm: 0.92–1.01 m (6H, CH_3), 1.76–1.87 m (4H, CH_2), 2.83 m (2H, CH_2), 3.12 m (2H, CH_2), 7.39–7.52 m (3H, Ph), 7.68–7.76 m (2H, Ph), 8.27 s (1H, =CHTe). ^{13}C NMR spectrum, δ_C, ppm: 13.72 (CH_3), 13.93 (CH_3), 21.33 (CH_2), 22.09 (CH_2), 36.29 (=C**C**H_2), 44.01 (=C**C**H_2), 121.81 (TeCH=), 127.44 (CH_{arom}), 128.94 (CH_{arom}), 129.09 (CH_{arom}), 131.56 (CH_{arom}), 133.85 (C_{arom}), 135.31 (ClC=), 147.42 (ClC=). Found, %: C 40.27; H 4.03; Cl 29.72. $C_{16}H_{20}Cl_4Te$. Calculated, %: C 39.89; H 4.18; Cl 29.44.

[(4*E*)-5-Chlorooct-4-en-4-yl][(*Z*)-2-chloro-2-phenylethenyl]tellane (4). A solution of 2 g (10.5 mmol) of $Na_2S_2O_5$ in 20 mL of water was added with stirring to a solution of 0.886 g (1.84 mmol) of tellane **3** in 25 mL of benzene, and the mixture was stirred for 2 h at room temperature. The organic layer was separated and dried over Na_2SO_4, the solvent was removed on a rotary evaporator, and the residue was dried under reduced pressure. Yield 0.711 g (94%), yellowish oily material. ^1H NMR spectrum, δ, ppm: 1.05–1.16 m (6H, CH_3), 1.72–1.85 m (4H, CH_2), 2.87 t (2H, CH_2), 2.96 t (2H, CH_2), 7.34–7.47 m (3H, Ph), 7.59–7.66 m (2H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 13.78 (CH_3), 14.74 (CH_3), 21.99 (CH_2), 23.19 (CH_2), 42.77 (=C**C**H_2), 45.77 (=C**C**H_2), 106.48 (TeCH=), 115.67 (TeC=), 126.51 (CH_{arom}), 128.71 (CH_{arom}), 128.76 (CH_{arom}); 138.04, 138.28, 138.87 (C_{arom}, ClC=). Found, %: C 47.06; H 5.09; Cl 16.98. $C_{16}H_{20}Cl_2Te$. Calculated, %: C 46.78; H 4.91; Cl 17.26.

The solvents were preliminarily dried and distilled just before use. The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 (^1H) and 100.61 MHz (^{13}C) using $CDCl_3$ as solvent and hexamethyldisiloxane as internal standard.

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