Cycloaddition of 2-pyridinetellurenyl chloride to alkenes

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The action of 2-pyridinetellurenyl chloride on alkenes results in the polar cycloaddition of the tellurium-centered electrophile at the multiple bond with the formation of 2,3-dihydro[1,3]tellurazolo[3,2-*a*]pyridinium derivatives.

Key words: 2-pyridinetellurenyl chloride, alkenes, polar cycloaddition, X-ray diffraction.

Organyltellurenyl halides RTeHal are known for more than half a century,[1—7] however, in contrast to organylsulfenyl- and organylselenenyl halides, addition of these reagents to multiple bonds is studied poorly. In the literature, there are only several examples of the reaction of aryltellurenyl halides with unsaturated carboxylic acids, which lead to the cyclization products with the ring closure by the oxygen atom of the carboxyl group in the molecule of unsaturated compound.[8,9]

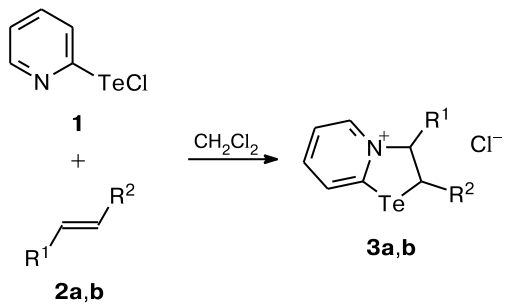
Recently,[10,11] we have synthesized 2-pyridinetellurenyl chloride (**1**), the first representative of hetarenetellurenyl halides containing a nitrogenous base as a hetaryl substituent, and shown that its reaction with alkenes leads to the heterocyclization products with the ring closure by the nitrogen atom of the pyridine ring of the starting reagent.[10]

To clarify regio- and stereochemistry, as well as a plausible mechanism of the heterocyclization found, in the present work we studied reactions of tellurenyl chloride **1** with styrene (**2a**), *tert*-butylethylene (**2b**), cyclopentene (**2c**), and norbornene (**2d**).

The reaction of tellurenyl chloride **1** with unsaturated compounds **2a**,**b** in dichloromethane at 20 °C was found to proceed regiospecifically to form the fused ring tellurium-nitrogen-containing heterocycles **3a** and **3b** in 97 and 94% yields, respectively (Scheme 1).

The reaction of compound **1** with alkenes **2c**,**d** under the same conditions leads to the products of *cis*-cycloaddition at the multiple bond, *viz.*, the polycyclic systems **3c** and **3d** in 92 and 95% yields, respectively (Scheme 2).

Scheme 1



R^1 = Ph, R^2 = H (**a**); R^1 = H, R^2 = Bu^t (**b**)

The structure of the synthesized compounds was inferred from the ^1H and ^{13}C NMR spectroscopic data and confirmed by the elemental analysis data.

The signals in the ^1H NMR spectra of compounds **3a**—**c** were assigned based on the obtained earlier spectral characteristics of cycloaddition products of hetarenesulfenyl chlorides to alkenes **2a**—**c**, whose structure was confirmed by X-ray crystallography.[12—14]

The structure of compound **3d** was established by X-ray diffraction studies (Fig. 1). Selected bond distances and bond angles are given in Table 1.

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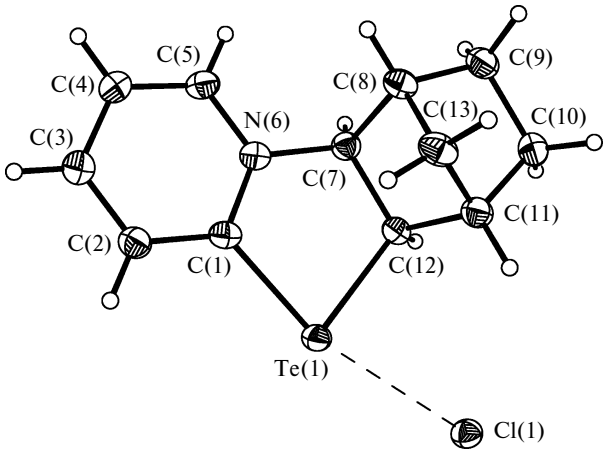


Fig. 1. Molecular structure of compound **3d**.

Scheme 2

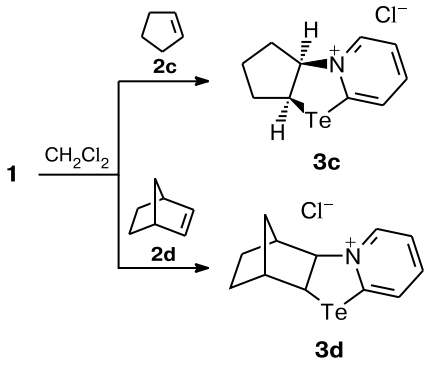


Table 1. Selected bond distances (*d*) and bond angles (ω) in the crystal of compound **3d**

Bond	*d*/Å	Angle	ω/deg
Te(1)—C(1)	2.115(2)	C(1)—Te(1)—C(12)	81.85(7)
Te(1)—C(12)	2.155(2)	Te(1)—C(1)—N(6)	114.26(13)
C(1)—N(6)	1.355(2)	C(1)—N(6)—C(7)	120.54(15)
N(6)—C(7)	1.502(3)	N(6)—C(7)—C(12)	112.58(14)
C(7)—C(12)	1.546(3)	Te(1)—C(12)—C(7)	110.40(12)

Compound **3d** is a salt containing the pyridinium cation and the chloride anion. The cation fragment Te(1)—C(1)—C(2)—C(3)—C(4)—C(5)—N(6)—C(7)—C(12) is virtually planar (an average deviation of the atoms from the mean square plane is 0.04 Å). The tellurium atom forms two additional short contacts with two chloride anions with the distances 3.078(1) and 3.343(1) Å, thus acquiring a distorted planar-square coordination. This type of interactions (Te...Hal) is characteristic of the large tellurium atom, and not only in the low-coordination compounds (for the case of intermolecular interactions of a dicoorditated tellurium atom with a chlorine atom, see recent the works[15—19]). Cations and anions in the crystal form chains along the axis *b* (Fig. 2) due to the existence of these attractive interactions Te...Cl.

The bicyclo[2.2.1]heptane fragment of the cation in compound **3d** has four asymmetric carbon atoms, C(7), C(8), C(11), and C(12). The absolute configurations of the indicated chiral centers are 7*S*,8*R*,11*S*,12*R*.

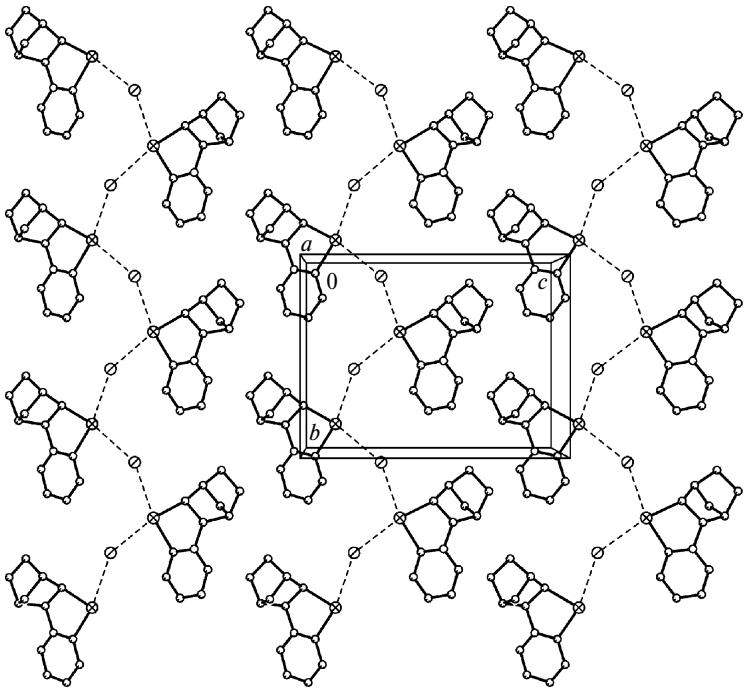
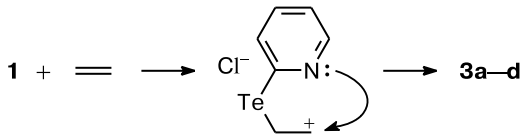


Fig. 2. Crystal packing of compound **3d**.

Earlier,[12—14,20] when we studied the tandem addition—cyclization processes in the reactions of hetarenesulfenyl- and hetareneselenenyl chlorides with alkenes, we found that the heterocyclization products with the ring closure by a nucleophilic active center of the reagent hetaryl fragment can be formed in two ways: the first way includes the ring closure directly in the Ad_E-process; in the second way, a cyclization product is formed as a result of intramolecular nucleophilic substitution in β-chloro sulfides or -selenides (the initial reaction products). In this connection, we monitored the reactions of tellurenyl chloride **1** with alkenes **2a—d** in deuterated dichloromethane by ^{1}H NMR spectroscopy. These experiments showed no formation of the 1,2-addition products of tellurenyl chloride **1** to the multiple bond even in trace amount.

In conclusion, the results obtained in this work allow us to draw a conclusion that the formation of compounds **3a—d** proceeds apparently by the scheme of polar cycloaddition,[12,21—23] which includes involvement of the **A** type intermediates (Scheme 3). Arising intermediates of this type can be attributed to the specific features of the tellurium-containing agent used, to be more specific, to the presence of coordination bonds involving tellurium atoms,[2,3,7,11] which shields these atoms preventing their reaction with the neighboring carbocationic center.

Scheme 3



A

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-600 spectrometer (600 and 150 MHz) in DMSO-d_6.

Styrene (**2a**), *tert*-butylethylene (**2b**), cyclopentene (**2c**), and norbornene (**2d**) were purchased from Acros Organics (Belgium), they were used freshly distilled. Dichloromethane was purified by distillation over P_2O_5.

Reaction of 2-pyridinetellurenyl chloride 1 with unsaturated compounds 2a—d (general procedure). A solution of unsaturated compound **2a—d** (1 mmol) in dichloromethane (10 mL) was added to a suspension of tellurenyl chloride **1** (0.24 g, 1 mmol) in dichloromethane (10 mL) at 20 °C with stirring. The solvent was evaporated *in vacuo* 24 h after the complete dissolution of tellurenyl chloride. Compounds **3a—d** were obtained after recrystallization of the residue from dichloromethane.

3-Phenyl-2,3-dihydro[1,3]tellurazolo[3,2-*a*]pyridin-4-ium chloride (3a). The yield was 97%. Yellow crystals, m.p. 172—174 °C. Found (%): C, 45.11; H, 3.45. $C_{13}H_{12}ClNTe$. Calculated (%): C, 45.22; H, 3.50. ^{1}H NMR, δ: 3.80 (dd, 1 H, H(2), J = 10.3 Hz, J = 7.3 Hz); 4.28 (dd, 1 H, H(2), J = 10.3 Hz, J = 7.3 Hz); 6.60 (t, 1 H, H(3), J = 7.3 Hz); 7.40 (m, 2 H, Ph); 7.48 (m, 3 H, Ph); 7.78 (dd, 1 H, H(6), J = 7.3 Hz, J = 5.9 Hz); 8.32 (t, 1 H, H(7), J = 7.3 Hz); 8.42 (d, 1 H, H(8), J = 7.3 Hz); 8.52 (d, 1 H, H(5), J = 5.9 Hz).

2-(*tert*-Butyl)-2,3-dihydro[1,3]tellurazolo[3,2-*a*]pyridin-4-ium chloride (3b). The yield was 94%. Yellow crystals, m.p. 188—190 °C. Found (%): C, 40.52; H, 4.87. $C_{11}H_{16}ClNTe$. Calculated (%): C, 40.61; H, 4.96. ^{1}H NMR, δ: 0.98 (s, 9 H, Bu^t); 4.44 (dd, 1 H, H(2), J = 7.3 Hz, J = 5.9 Hz); 5.16 (dd, 1 H, H(3), J = 13.2 Hz, J = 7.3 Hz); 5.42 (dd, 1 H, H(3), J = 13.2 Hz, J = 5.9 Hz); 7.81 (dd, 1 H, H(6), J = 7.3 Hz, J = 5.9 Hz); 8.27 (dd, 1 H, H(7), J = 8.8 Hz, J = 7.3 Hz); 8.35 (d, 1 H, H(8), J = 8.8 Hz); 9.09 (d, 1 H, H(5), J = 5.9 Hz).

***cis*-2,3,3a,9a-Tetrahydro-1*H*-cyclopenta[4,5][1,3]tellurazolo[3,2-*a*]pyridin-9-ium chloride (3c).** The yield was 92%. Yellow crystals, m.p. 135—137 °C. Found (%): C, 38.68; H, 3.79. $C_{10}H_{12}ClNTe$. Calculated (%): C, 38.84; H, 3.91. ^{1}H NMR, δ: 1.70 (m, 2 H, CH_2); 2.07 (m, 2 H, CH_2); 2.24 (m, 1 H, CH_2); 2.41 (m, 1 H, CH_2); 4.65 (td, 1 H, H(3a), J = 8.0 Hz, J = 4.7 Hz); 5.78 (td, 1 H, H(9a), J = 8.5 Hz, J = 3.8 Hz); 7.75 (td, 1 H, H(7), J = 6.2 Hz, J = 4.5 Hz); 8.22 (d, 2 H, H(5), H(6), J = 4.4 Hz); 8.97 (d, 1 H, H(8), J = 6.2 Hz).

***exo-cis*-9-Tellurium-3-azoniatetracyclo[9.2.1.0^{2,10}.0^{3,8}]tetradeca-3(8),4,6-triene chloride (3d).** The yield was 95%. Yellow crystals, m.p. 230—232 °C. Found (%): C, 42.88; H, 4.15. $C_{12}H_{14}ClNTe$. Calculated (%): C, 42.99; H, 4.21. ^{1}H NMR, δ: 1.34 (d, 1 H, H_{syn}(14), J = 10.8 Hz); 1.39 (m, 1 H, H(12)); 1.52 (m, 1 H, H(12)); 1.68 (d, 1 H, H_{anti}(14), J = 10.8 Hz); 1.71 (m, 2 H, H(13)); 2.61 (s, 1 H, H(11)); 2.82 (s, 1 H, H(1)); 4.12 (d, 1 H, H(10), J = 8.4 Hz); 5.32 (d, 1 H, H(2), J = 8.4 Hz); 7.70 (dd, 1 H, H(5), J = 7.5 Hz, J = 6.2 Hz); 8.01 (dd, 1 H, H(6), J = 8.0 Hz, J = 7.5 Hz); 8.20 (d, 1 H, H(7), J = 8.0 Hz); 8.93 (d, 1 H, H(4), J = 6.2 Hz). ^{13}C NMR, δ: 25.71 (C(12)); 29.41 (C(13)); 31.84 (C(14)); 32.84 (C(10)); 45.97 (C(11)); 48.16 (C(1)); 82.78 (C(2)); 123.99 (C(5)); 132.61 (C(7)); 141.45 (C(6)); 145.22 (C(4)).

X-ray diffraction studies of compound 3d. Parameters of a unit cell and intensities of 17726 reflections were measured on a Bruker SMART APEX-II CCD automatic three-circle diffractometer (Mo-Kα-irradiation, graphite monochromator, φ- and ω-scan technique, θ_{max} = 32.7°). For the data obtained, the absorption of X-ray irradiation was applied using the SADABS program.[24] The structure of compound **3d** was solved by the direct method and refined by the full-matrix least squares method in anisotropic approximation for nonhydrogen atoms. All the hydrogen atoms, whose positions were calculated geometrically, were included into the refinement in isotropic approximation with the fixed positional (the riding model) and thermal parameters. The absolute configuration of the asymmetric atoms in compound **3d** was determined objectively through the refinement of the Fleck parameter, which is equal to 0.116(15). A slightly overrated Fleck parameter is explained by the specific (close to the centrosymmetric) arrangement of the heavy tellurium atoms. All the calculations were performed using the SHELXTL program package.[25] The crystals $C_{12}H_{14}ClNTe$ at 100 K are orthorhombic, a = 9.3956(3) Å, b = 9.7605(3) Å, c = 12.9619(4) Å, V = = 1188.68(6) Å^3, Z = 4, space group $P2_12_12_1$, d_{calc} = 1.874 g cm^{-3}, $F(000)$ = 648, μ = 2.694 mm^{-1}, the residual electron density 0.978/−0.298 e Å^{-3}. The final divergence factors R_1 = 0.0189 for 4200 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.0450 for all the 4368 independent reflections. Tables of the atomic

coordinates, bond distances, bond and torsional angles, and parameters of anisotropic displacements for compound **3d** were deposited with the Cambrige Structural Database (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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