Polar cycloaddition of 2-pyridinetellurium trichloride to multiple bonds*

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A reaction of 2-pyridinetellurium trichloride with unsaturated hydrocarbons leads to [1,3]tellurazolo[3,2-*a*]pyridinium-4 derivatives — the products of polar cycloaddition of tellurium-containing electrophile at the multiple bond.

Key words: 2-pyridinetellurium trichloride, alkenes, acetylenes, cycloaddition, [1,3]tellurazolo[3,2-*a*]pyridinium-4 derivatives.

It is known that the reaction of arenetellurium trihalides $ArTeHal_3$ with alkenes and acetylenes usually gives the products of 1,2-addition at the multiple bonds, β-haloalkyl(vinyl)tellurium dihalides[1—5] or the products of transannular cyclization with the ring closure by the electron-donating center of the functional group containing in the molecule of the unsaturated substrate, lactones, ordinary cyclic ethers, pyrrolidine and piperidine derivatives.[1,2,6—11]

In the present work, we synthesized 2-pyridinetellurium trichloride (**1**), the first representative of hetarenetellurium trihalides containing a nitrogen base as the hetaryl substituent and studied its reactions with norbornene (**2**), cyclopentene (**3**), and *p*-methoxyphenylacetylene (**4**). The indicated reactions in dichloromethane at 20 °C were found to result in the formation of the heterocyclization products with the ring closure by the nitrogen atom of the pyridine ring in the starting electrophilic agent, *i.e.*, salts **5**—**7**, in 95, 82, and 96% yields, respectively (Scheme 1).

It can be suggested that the formation of the condensed heterocyclic systems **5**—**7** follows the scheme of polar cycloaddition similarly to the reactions of 2-pyridinetellurenyl chloride with alkenes studied by us earlier[12], since we did not observe the formation of the 1,2-addition products of reagent **1** to unsaturated compounds **2**—**4** even in the trace amounts.

The structure of compounds obtained was confirmed by the ^1H NMR spectroscopic, ESI mass spectrometric, and elemental analysis data. The signals in the ^1H NMR spectra were assigned based on the spectral characteristics of cycloaddition products of chalcogen-centered electrophiles to unsaturated compounds obtained by us earlier, whose structure was confirmed by X-ray crystallography.[12—16]

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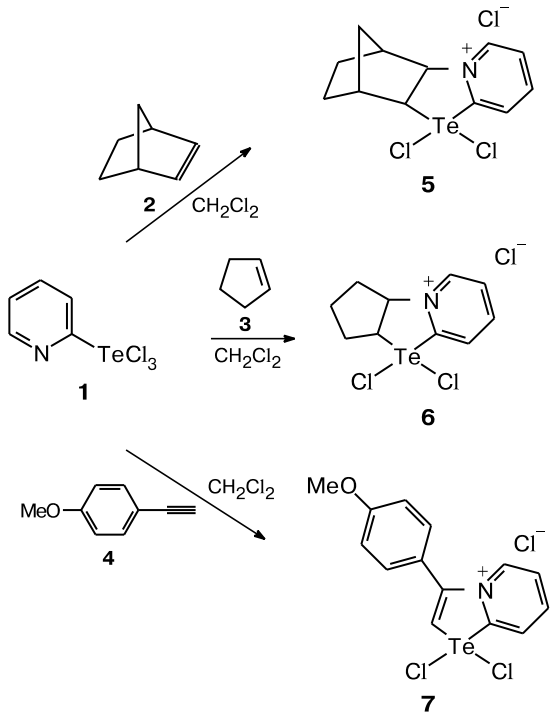
Scheme 1



Experimental

Di(2-pyridyl) ditelluride was obtained according to the known procedure.[17] Other reagents were purchased from Acros Organics (Belgium) and used without preliminary purification. The solvent CH_2Cl_2 was purified by distillation over P_2O_5. ^1H NMR spectra of were recorded on a Bruker AM-300 spectrometer (300 MHz) in DMSO-d_6. Mass spectra ESI were obtained on a Finnigan MAT INCOS 50 quadrupole mass spectrometer (70 eV). In the mass spectra, the *m/z* values for the peaks of the maximal intensity in the Te-containing isotope cluster are reported.

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2-Pyridinetellurium trichloride (1). A solution of sulfuryl chloride (0.1 g, 0.75 mmol) in dichloromethane (5 mL) was added to a solution of di(2-pyridyl) ditelluride (0.103 g, 0.25 mmol) in dichloromethane (5 mL) at 20 °C. After 1 h, compound **1** was filtered off as white crystals. The yield was 0.155 g (97%), m.p. 240—242 °C (decomp.). Found (%): C, 19.18; H, 1.24; N, 4.42. $C_5H_4Cl_3NTe$. Calculated (%): C, 19.24; H, 1.29; N, 4.49. MS, *m/z* (I_{rel} (%)): 313 $[M]^{+\cdot}$ (1.6), 278 $[C_5H_4NTeCl_2]^{+\cdot}$ (2.0); 243 $[C_5H_4NTeCl]^{+\cdot}$ (4.1); 208 $[C_5H_4NTe]^{+\cdot}$ (3.4); 200 $[TeCl_2]^{+\cdot}$ (3.3); 196 $[C_4H_3NTe]^{+\cdot}$ (1.8); 165 $[TeCl]^+$ (4.1); 130 $[Te]^{+\cdot}$ (7.9); 113 $[C_5H_4NCl]^{+\cdot}$ (0.6); 78 $[C_5H_4N]^+$ (100); 51 $[C_4H_3]^+$ (47.6); 39 $[C_3H_3]^+$ (7.8); 38 $[HCl]^{+\cdot}$ (1.6); 36 $[HCl]^{+\cdot}$ (4.8).

Reaction of tellurium trichloride 1 with unsaturated compounds 2—4 (general procedure). A solution of unsaturated compound **2**—**4** (0.25 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of tellurium trichloride (**1**) (0.078 g, 0.25 mmol) in CH_2Cl_2 (10 mL) at 20 °C. The reaction mixture was kept for 24 h at 20 °C, the solvent was evaporated at reduced pressure. Compounds **5**—**7** were obtained after recrystallization of the residue from CH_2Cl_2.

***exo-cis*-9,9-Dichloro-9-tellura-3-azoniatetracyclo-[9.2.1.0^{2,10}.0^{3,8}]tetradeca-3,5,7-triene chloride (5).** The yield was 95%, white crystals, m.p. 243—245 °C. Found (%): C, 35.37; H, 3.41; N, 3.39. $C_{12}H_{14}Cl_3NTe$. Calculated (%): C, 35.48; H, 3.47; N, 3.45. ^{1}H NMR, δ: 1.27 (d, 1 H, H_{syn}(14), J = 11.7 Hz); 1.37 (m, 2 H, H(12)); 1.63 (d, 1 H, H_{anti}(14), J = 11.7 Hz); 1.80 (m, 2 H, H(13)); 3.09 (s, 1 H, H(11)); 3.12 (s, 1 H, H(1)); 3.86 (d, 1 H, H(10), J = 7.3 Hz); 5.70 (d, 1 H, H(2), J = 7.3 Hz); 8.22 (dd, 1 H, H(5), J = 7.3 Hz, J = 5.9 Hz); 8.58 (t, 1 H, H(6), J = 7.3 Hz); 8.66 (d, 1 H, H(7), J = 7.3 Hz); 9.32 (d, 1 H, H(4), J = 5.9 Hz). MS, *m/z* (I_{rel} (%)): 370 $[C_{12}H_{14}NTeCl_2]^+$ (0.4); 300 $[C_{12}H_{14}NTe]^+$ (0.6); 278 $[C_5H_4NTeCl_2]^+$ (10.2); 243 $[C_5H_4NTeCl]^{+\cdot}$ (14.6); 208 $[C_5H_4NTe]^+$ (7.0); 200 $[TeCl_2]^{+\cdot}$ (10.2); 130 $[Te]^{+\cdot}$ (15.1); 165 $[TeCl]^+$ (13.1); 113 $[C_5H_4NCl]^{+\cdot}$ (9.9·); 94 $[C_7H_{10}]^+$ (10.6); 91 $[C_7H_7]^+$ (7.9); 78 $[C_5H_4N]^+$ (85.6); 66 $[C_5H_6]^{+\cdot}$ (100); 51 $[C_4H_3]^+$ (48.7); 39 $[C_3H_3]^+$ (43.1); 36 $[HCl]^{+\cdot}$ (13).

***cis*-4,4-Dichloro-2,3,3a,9a-tetrahydro-1*H*-cyclopenta[4,5]-[1,3]tellurazolo[3,2-*a*]pyridinium-9 chloride (6).** The yield was 82%, yellow crystals, m.p. 57—58 °C. Found (%): C, 31.51; H, 3.11; N, 3.60. $C_{10}H_{12}Cl_3NTe$. Calculated (%): C, 31.59; H, 3.18; N 3.68. ^{1}H NMR, δ: 1.71 (m, 2 H, CH_2); 2.07 (m, 1 H, CH_2); 2.42 (m, 1 H, CH_2); 2.63 (m, 1 H, CH_2); 2.89 (m, 1 H, CH_2); 4.57 (dd, 1 H, H(3a), J = 15.8 Hz, J = 8.5 Hz); 6.27 (dd, 1 H, H(9a), J = 15.8 Hz, J = 8.5 Hz); 8.23 (dd, 1 H, H(7), J = 7.3 Hz, J = 6.1 Hz); 8.59 (dd, 1 H, H(6), J = 8.0 Hz, J = 7.3 Hz); 8.69 (d, 1 H, H(5), J = 7.3 Hz); 9.24 (d, 1 H, H(8), J = 6.1 Hz). MS, *m/z* (I_{rel} (%)): 278 $[C_5H_4NTeCl_2]^+$ (2.9); 243 $[C_5H_4NTeCl]^{+\cdot}$ (16.4); 208 $[C_5H_4NTe]^+$ (10.1); 200 $[TeCl_2]^{+\cdot}$ (4.3); 165 $[TeCl]^+$ (10.4); 130 $[Te]^{+\cdot}$ (17.1); 113 $[C_5H_4NCl]^{+\cdot}$ (9.4); 78 $[C_5H_4N]^+$ (100); 67 $[C_5H_7]^+$ (77.9); 51 $[C_4H_3]^+$ (37.4); 39 $[C_3H_3]^+$ (38.6); 36 $[HCl]^{+\cdot}$ (33.2).

1,1-Dichloro-3-(4-methoxyphenyl)[1,3]tellurazolo[3,2-*a*]-pyridinium-4 chloride (7). The yield was 96%, orange crystals, m.p. 130—132 °C. Found (%): C, 37.74; H, 2.68; N, 3.10. $C_{14}H_{12}Cl_3NOTe$. Calculated (%): C, 37.85; H, 2.72; N, 3.15. ^{1}H NMR, δ: 3.87 (s, 3 H, CH_3O); 7.18 (d, 2 H, H(3′), H(5′)), ^3J = 8.8 Hz); 7.57 (d, 2 H, H(2′), H(6′)), ^3J = 8.8 Hz); 7.72 (t, 1 H, H(7), ^3J = 7.3 Hz); 7.98 (t, 1 H, H(6), ^3J = 7.3 Hz); 8.78 (s, 1 H, H(2)); 8.86 (d, 1 H, H(8), ^3J = 7.3 Hz); 9.02 (d, 1 H, H(5), ^3J = 7.3 Hz).

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References

1. M. M. Campos, N. Petragnani, *Tetrahedron Lett.*, 1959, **1**, 11.
2. M. M. Campos, N. Petragnani, *Tetrahedron*, 1962, **18**, 521.
3. B. Borecka, T. S. Cameron, M. A. Malik, B. C. Smith, *Can. J. Chem.*, 1994, **72**, 1844.
4. X. Huang, Y.-P. Wang, *Tetrahedron Lett.*, 1996, **37**, 7417.
5. Y. Torubaev, P. Mathur, A. A. Pasynskii, *J. Organomet. Chem.*, 2010, **695**, 1300.
6. N. Petragnani, H. A. Stefani, *Tellurium in Organic Synthesis — Best Synthetic Methods*, 2nd ed., Academic Press, London, 2007, 398 p.
7. J. V. Comasseto, N. Petragnani, *Synth. Commun.*, 1983, **13**, 889.
8. J. V.Comasseto, H. M. C. Ferraz, N. Petragnani, C. A. Brandt, *Tetrahedron Lett.,* 1987, **28**, 5611.
9. J. V. Comasseto, M. V. A. Grazini, *Synth. Commun.*, 1992, **22**, 949.
10. M. H. C. Ferraz, M. K. Sano, A. C. Scalfo, *Synlett,* 1999, **5**, 567.
11. N. X. Hu, Y. Aso, T. Otsuba, F. Ogura, *Chem. Lett.*, 1987, 1327.
12. A. V. Borisov, Zh. V. Matsulevich, V. K. Osmanov, G. N. Borisova, V. I. Naumov, G. Z. Mammadova, A. M. Maharramov, V. N. Khrustalev, V. V. Kachala, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 91 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2012, 89].
13. A. V. Borisov, Zh. V. Matsulevich, V. K. Osmanov, G. N. Borisova, G. Z. Mammadova, A. M. Maharramov, V. N. Khrustalev, *Russ. Chem. Bull.* (*Int. Ed.*), 2011, **60**, 2057 [*Izv. Akad. Nauk*, *Ser. Khim.,* 2011, 2020].
14. A. V. Borisov, Zh. V. Matsulevich, V. K. Osmanov, G. N. Borisova, G. Z. Mammadova, A. M. Maharramov, V. N. Khrustalev, *Khim. Geterotsikl. Soedin.*, 2012, 1034 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2012].
15. A. V. Borisov, Zh. V. Matsulevich, V. K. Osmanov, G. N. Borisova, G. Z. Mammadova, A. M. Maharramov, V. N. Khrustalev, *Khim. Geterotsikl. Soedin.*, 2012, 1167 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2012].
16. A. V. Borisov, Zh. V. Matsulevich, V. K. Osmanov, G. N. Borisova, G. Z. Mammadova, A. M. Maharramov, V. N. Khrustalev, *Khim. Geterotsikl. Soedin.*, 2012, 1180. [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2012].
17. L. Engman, M. P. Cava, *Organometallics*, 1982, **1**, 470.

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