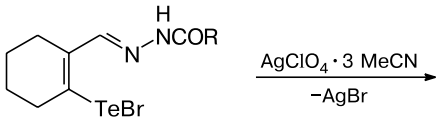
# Synthesis of 2-aroylamino-4,5,6,7-tetrahydro-1,2-benzotellurazolium perchlorates

*A. V. Zakharov, I. D. Sadekov,* and V. I. Minkin*

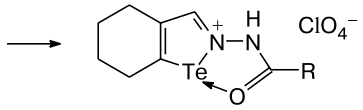
*Research Institute of Physical and Organic Chemistry, Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 43 4667. E-mail: sadek@ipoc.rsu.ru*

Isotellurazolium salts and their benzo analogs are synthesized in two alternative methods. *N*-Methylisotellurazolium[1] and *N*-methylbenzoisotellurazolium[2] iodides have been obtained by reactions of methyl iodide with the corresponding heterocycles. *N*-Arylisotellurazolium[1] and *N*-arylbenzoisotellurazolium[3] perchlorates have been obtained by treatment of solutions of 2-tellurenylvinylaldimines and 2-chlorotellurenylbenzalanilines in acetone with silver perchlorate.

We employed an analogous approach for the synthesis of novel 2-aroylamino-4,5,6,7-tetrahydro-1,2-benzotellurazolium perchlorates (**1**). Aroylhydrazones **2** used as precursors of compounds **1** are easily prepared by brief refluxing of equimolar amounts of 2-(methyldibromotelluro)cyclohexene-1-carbaldehyde and aromatic[4] and heterocyclic carbohydrazides. Treatment of aroylhydrazones **2** with a complex of silver perchlorate with acetonitrile yielded compounds **1** in 87—92% yields.




**2**




**1**

R = 4-$BrC_6H_4$ (**a**), 4-$MeC_6H_4$ (**b**), 4-Py (**c**)

The structures of the compounds obtained were proven by $^1$H NMR spectroscopy. Signals for the H(3) atom in the $^1$H NMR spectra of heterocycles **1** (8.98 (**a**), 8.53 (**b**), and 9.10 (**c**)) are shifted downfield by 0.12—0.77 ppm compared to analogous signals in the $^1$H NMR spectra of hydrazones **2** (9.13 (**a**), 9.30 (**b**), and 9.35 (**c**)). The cyclization of tellurenyl bromides **2** into heterocycles **1** is evident from the $^{125}$Te chemical shifts for compounds **2a** and **1a**. The $^{125}$Te NMR spectrum of tellurenyl bromide **2a** shows a signal at δ 1534.8, which is close to the $^{125}$Te chemical shifts for *N*-arylimines of 2-bromotellurenylcyclohexene-1-carbaldehyde *cyclo*-$C_6H_8$(TeBr)CH=NAr (δ 1424—1428)[5]. However, in the $^{125}$Te NMR spectrum of heterocycle **1a**, a resonance signal appears at δ 744.8.

Compounds **1** can be stabilized by intramolecular O→Te coordination bond; a similar bond (2.831 Å) has been found[5] in hydrazone **2a**.

## Experimental

$^1$H and $^{125}$Te NMR spectra were recorded on a Varian Unity-300 spectrometer.

Hydrazone **2a** was prepared as described earlier.[4]

**(4-Methylbenzoyl)hydrazone of 2-bromotellurenylcyclohex-1-ene-1-carbaldehyde (2b).** A mixture of 2-(methyldibromotelluro)cyclohexene-1-carbaldehyde (4.12 g, 10 mmol) and 4-methylbenzohydrazide (1.50 g, 10 mmol) in methanol (35 mL) was refluxed for 30 min until a precipitate of hydrazone **2b** formed. The reaction mixture was cooled and the precipitate was filtered off and dried to give compound **2b** (77%) as bright yellow crystals, m.p. 264 °C (from toluene—hexane (1 : 2)). Found (%): C, 40.22; H, 3.65. $C_{15}H_{17}BrN_2OTe$. Calculated (%): C, 40.14; H, 3.82. $^1$H NMR ($CDCl_3$), δ: 1.80—3.00 (m, 8 H, $(CH_2)_4$); 2.40 (s, 3 H, $CH_3$); 7.29 (d, 2 H, $C_6H_4$, $J$ = 7.6 Hz); 7.76 (d, 2 H, $C_6H_4$, $J$ = 7.6 Hz); 8.53 (s, 1 H, CH=N); 9.82 (s, 1 H, NH).

**Isonicotinoylhydrazone of 2-(bromotellurenyl)cyclohexene-1-carbaldehyde (2c)** was obtained analogously as yellow crystals. The yield was 85%, m.p. 268 °C (from toluene—hexane (1 : 2)). Found (%): C, 35.61; H, 3.11. $C_{13}H_{14}BrN_3OTe$. Calculated (%): C, 35.83; H, 3.24. $^1$H NMR (DMSO-$d_6$), δ: 1.80—3.00 (m, 8 H, $(CH_2)_4$); 8.15 (d, 2 H, $C_5H_4N$, $J$ = 6.44 Hz); 8.85 (d, 2 H, $C_5H_4N$, $J$ = 6.44 Hz); 9.10 (s, 1 H, CH=N).

**2-Isonicotinoylamino-4,5,6,7-tetrahydro-1,2-benzotellurazolium perchlorate (1c).** A solution of $AgClO_4 \cdot 3CH_3CN$ (0.758 g, 2.3 mmol) in acetone (5 mL) was added to a stirred suspension of hydrazone (**2c**) (1.0 g, 2.3 mmol) in acetone (10 mL). The precipitate of AgBr was filtered off and the filtrate was diluted with ether (10 mL). Crystallization at –15 °C gave product **1c** (92%) as yellow crystals, m.p. 245—247 °C. Found (%): C, 34.18; H, 3.23. $C_{13}H_{14}ClN_3O_5Te$. Calculated (%): C, 34.29; H, 3.11. $^1$H NMR (DMSO-$d_6$), δ: 1.80—3.00 (m, 8 H, $(CH_2)_4$); 8.15 (d, 2 H, $C_5H_4N$, $J$ = 6.44 Hz); 8.85 (d, 2 H, $C_5H_4N$, $J$ = 6.44 Hz); 9.35 (s, 1 H, H(3)).

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Compounds **1a** and **1b** were obtained analogously.

**2-(4-Bromobenzoylamino)-4,5,6,7-tetrahydro-1,2-benzotellurazolium perchlorate (1a).** The yield was 87%, yellow crystals, m.p. 193—195 °C (from acetone—ether). Found (%): C, 31.47; H, 2.51. $C_{14}H_{14}BrClN_2O_5Te$. Calculated (%): C, 31.53; H, 2.65. $^1$H NMR (DMSO-$d_6$), δ: 1.78—2.91 (m, 8 H, $(CH_2)_4$); 7.76 (d, 2 H, $C_6H_4$, $J$ = 8.57 Hz); 7.91 (d, 2 H, $C_6H_4$, $J$ = 8.57 Hz); 9.13 (s, 1 H, H(3)).

**2-(4-Methylbenzoylamino)-4,5,6,7-tetrahydro-1,2-benzotellurazolium perchlorate (1b).** The yield was 87%, yellow crystals, m.p. 186—189 °C (from acetone—ether). Found (%): C, 38.51; H, 3.53. $C_{15}H_{17}ClN_2O_5Te$. Calculated (%): C, 38.46; H, 3.67. $^1$H NMR ($CDCl_3$), δ: 1.80—3.00 (m, 8 H, $(CH_2)_4$); 2.40 (s, 3 H, Me); 7.29 (d, 2 H, $C_6H_4$, $J$ = 8.28 Hz); 7.92 (d, 2 H, $C_6H_4$, $J$ = 8.28 Hz); 9.30 (s, 1 H, H(3)).

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