

SHORT
COMMUNICATIONS

Cyclization of 2-Butyltellurobenzyl Haloacetates*

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The syntheses of tellurocoumarin [1], telluroisocoumarin [2], and 1,4-benzotellurazin-3*H*-one [3] were performed by intramolecular alkylation at tellurium atom with subsequent elimination of haloalkanes from the intermediately formed telluronium salts. We used a similar approach to the synthesis of derivatives of a new heterocyclic system, 2,3-benzo-1-tellur-5-oxacycloheptan-6-one. The treatment of a benzene solution of 2-butyltellurobenzyl alcohol [4] with haloacetyl chlorides we obtained haloacetates **Ia, b** characterized as the corresponding dihalides **IIa, b** isolated in 60–85% yield.

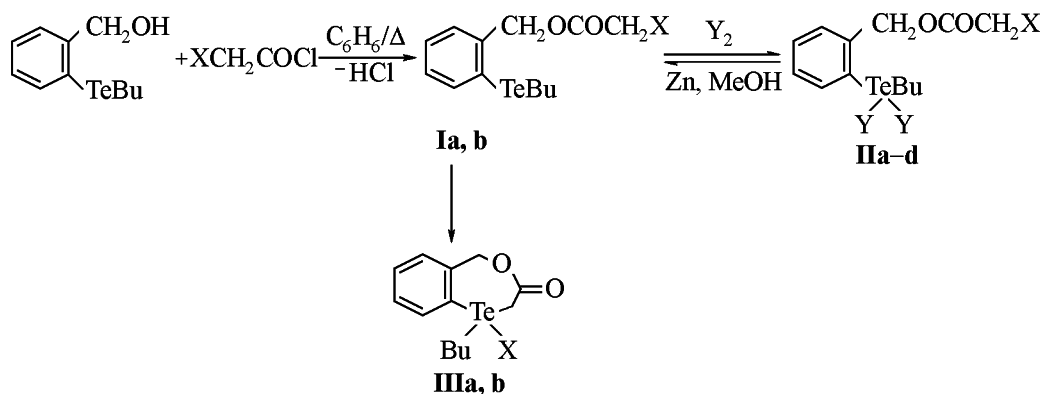
The composition and structure of σ -telluranes (**II**) were proved by elemental analysis and ^1H NMR spectra where the signals of CH_2O and CH_2X ($\text{X} = \text{Cl}, \text{Br}$) groups appeared at 4.45–4.50 and 5.64–5.76 ppm respectively.

Tellurodibromides **IIb, d** purified by crystallization were reduced with excess zinc powder in methanol. Thus prepared haloacetates **I** on removing the excess reducing agent and part of solvent slowly cyclized at room temperature into the derivatives of 2,3-benzo-

1-tellur-5-oxacycloheptan-6-one **IIIa, b**. In this process unlike the syntheses of the mentioned six-membered tellurium-containing heterocycles no elimination of butyl halides occurred both at room temperature and at boiling in toluene solution. By analogy with the earlier studied [4] derivatives of 5*H*-benzo-2,1-oxatellurool we described the structure of compounds obtained as 1-butyl-1-halo-2,3-benzo-1-tellur-5-oxacycloheptan-6-one (**III**).

The cyclic structure of compounds **IIIa, b** was unambiguously proved by appearance of the methylene protons signal from the group attached to tellurium atom as an *AB*-quartet. The yield of heterocycles **III** increased at going from chloride (23%) to bromide (40%) in keeping with growing nucleophilicity of the initial substrates **I**.

2-Butylhalotellurobenzyl haloacetates IIa-d. To a boiling solution of 0.03 mol of 2-butyltellurobenzyl alcohol in 100 ml of benzene was added dropwise at stirring a solution of 0.31 mol of the corresponding acyl chloride. The solution was boiled for 1 h, 60 ml of solvent was distilled off, the residual



I, III, X = Cl (a), Br (b); II, X = Cl (a, b), Br (c, d); Y = Cl (a, c), Br (b, d).

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solution was cooled to 0°C, and at stirring thereto was passed a flow of dry gaseous chlorine for 10–15 min, or was added a solution of 0.03 mol of bromine. The solvent was distilled off till ~20 ml volume of solution, and at 0°C was added while stirring 50 ml of ether. The precipitated crystals were filtered off, washed with petroleum ether, dried, and recrystallized from acetone.

2-Butyldichlorotellurobenzyl chloroacetate (IIa).

Yield 62%, colorless crystals, mp 102–103°C (from benzene). ¹H NMR spectrum, δ, ppm: 1.12–4.15 m (9H, Bu), 4.49 s (2H, CH₂O), 5.75 s (2H, CH₂Cl), 7.75–8.28 m (4H arom). Found, %: C 35.12; H 3.71. C₁₃H₁₇Cl₃O₂Te. Calculated, %: C 35.55; H 3.90.

2-Butyldichlorotellurobenzyl bromoacetate (IIb).

Yield 65%, colorless crystals, mp 97–98°C (from benzene). ¹H NMR spectrum, δ, ppm: 1.10–4.16 m (9H, Bu), 4.50 s (2H, CH₂O), 5.76 s (2H, CH₂Cl), 7.73–8.24 m (4H arom). Found, %: C 33.01; H 3.55. C₁₃H₁₇BrCl₂O₂Te. Calculated, %: C 32.89; H 3.61.

2-Butyldibromotellurobenzyl chloroacetate (IIc).

Yield 70%, yellow crystals, mp 114–116°C (from benzene). ¹H NMR spectrum, δ, ppm: 1.08–4.04 m (9H, Bu), 4.45 s (2H, CH₂O), 5.64 s (2H, CH₂Cl), 7.62–8.19 m (4H arom). Found, %: C 29.28; H 3.10. C₁₃H₁₇Br₂ClO₂Te. Calculated, %: C 29.56; H 3.25.

2-Butyldibromotellurobenzyl bromoacetate (IIa).

Yield 85%, yellow crystals, mp 109–111°C (from benzene). ¹H NMR spectrum, δ, ppm: 1.13–4.09 m (9H, Bu), 4.48 s (2H, CH₂O), 5.70 s (2H, CH₂Cl), 7.60–8.15 m (4H arom). Found, %: C 27.50; H 3.05. C₁₃H₁₇Br₃O₂Te. Calculated, %: C 27.70; H 3.04.

1-Butyl-1-halo-2,3-benzo-1-tellur-5-oxacycloheptan-6-ones III. To a suspension of 0.01 mol of 2-haloacetate **IIc, d** in 50 ml of methanol at boiling and vigorous stirring was added by small portions 1.3 g (0.02 mol) of zinc powder. After 30 min of boiling the reaction mixture was cooled, diluted

with 100 ml of water, and the reaction product was extracted into benzene (3 × 20 ml). The benzene layer of light-yellow color was separated, washed with water, dried on MgSO₄, and the solvent was evaporated. The residue was dissolved in 30 ml of methanol and maintained at room temperature for 3 days. The precipitated crystals were filtered off, dried, and recrystallized from a minimal amount of acetone.

1-Butyl-1-chloro-2,3-benzo-1-tellur-5-oxacycloheptan-6-one (IIIa).

Yield 23%. Yellowish crystals, mp 96–98°C (from acetone). ¹H NMR spectrum, δ, ppm: 0.88–3.12 m (9H, Bu), 3.00 s (2H, CH₂O), 5.39 d, 5.69 d (2H, CH₂Te), 7.44–8.37 m (4H arom). Found, %: C 42.08; H 4.72. C₁₃H₁₇ClO₂Te. Calculated, %: C 42.38; H 4.66.

1-Butyl-1-bromo-2,3-benzo-1-tellur-5-oxacycloheptan-6-one.

Yield 40%. Yellowish crystals, mp 107–109°C (from acetone). ¹H NMR spectrum, δ, ppm: 0.84–1.17 m (9H, Bu), 2.98 s (2H, CH₂O), 5.35 d, 5.65 d (2H, CH₂Te), 7.40–8.42 m (4H arom). Found, %: C 38.02; H 4.00. C₁₃H₁₇BrO₂Te. Calculated, %: C 37.82; H 4.16.

¹H NMR spectra of compounds **II, III** in acetone-*d*₆ were registered at 18–20°C on spectrometer Varian-Unity 300 (300 MHz).

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