Synthesis of 2-substituted benzo-1,3-ditelluroles

P. I. Gadzhieva[a]* *and I. D. Sadekov*[b]

[a] *Department of Chemistry, Dagestan State University, 43a ul. M. Gadzhieva, 367025 Makhachkala, Russian Federation. Fax: +7 (872 2) 68 2332. E-mail: israpil_pig@yahoo.com*

[b] *Research Institute of Physical and Organic Chemistry, Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 28 5667. E-mail: sadek@ipoc.rnd.runnet.ru*

A method for the synthesis of 2-phenylbenzo-1,3-ditellurole by the reaction of disodium *o*-benzeneditellurolate with benzylidene chloride was proposed. 2-Methylbenzo-1,3-ditellurole and benzo-1,3-ditellurole-2-carboxylic acid were prepared by the reaction of 2-lithiobenzo-1,3-ditellurole with MeI and CO_2, respectively.

Key words: 2-substituted benzo-1,3-ditelluroles, synthesis, lithiation, reduction.

Unlike sulfur and selenium analogs,[1] benzo-1,3-ditelluroles are poorly studied heterocyclic compounds. Syntheses of benzo-1,3-ditellurole[2,3] and 2-butoxybenzo-1,3-ditellurole are based on the reactions of disodium *o*-benzeneditellurolate with CH_2Br_2[2,3] and $BuOCHCl_2$,[4] respectively; some reactions of these compounds have been studied.

In the present report, we describe methods for the preparation of previously unknown 2-methyl- and 2-phenylbenzo-1,3-ditelluroles and benzo-1,3-ditellurole-2-carboxylic acid.

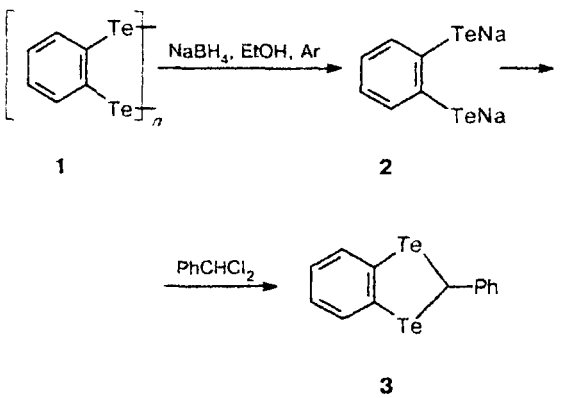
2-Phenylbenzo-1,3-ditellurole (**3**) was synthesized by the reaction of disodium *o*-benzeneditellurolate (**2**) with benzylidene chloride in ethanol. Salt **2** was prepared by the reduction of poly(*o*-phenylene ditelluride) (**1**) in the same solvent in an atmosphere of Ar according to the known procedures.[2,3] The yield of heterocycle **3** was 12—15% (Scheme 1).

A possible reason for the comparatively low yield of compound **3** is low nucleophilicity of the intermediate anion **2** due to complex formation of the latter with trialkyl borate formed from $NaBH_4$. This assumption is favored by the data from the previously published work.[5] The $PhSe^-$ anion obtained by the reduction of diphenyl diselenide with $NaBH_4$ in THF/EtOH exists as the complex anion $[PhSeB(OEt)_3]^-$ and is a much weaker nucleophile than the "free" benzeneselenolate anion generated by the reaction of Ph_2Se_2 with Na in THF.

Of some approaches for the generation of free dianion **2**, that based on the reduction of polytelluride **1** by the N_2H_4—NaOH system in DMF is the most convenient in the preparative aspect.

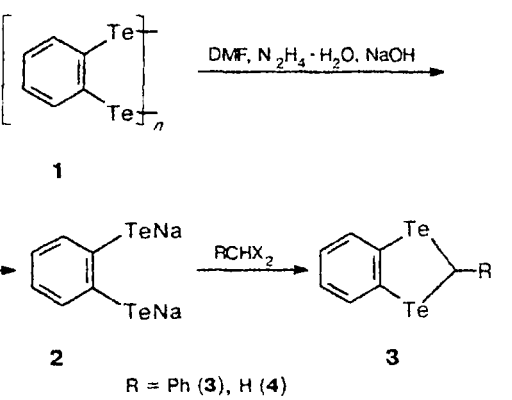
The reactions of the thus prepared ditellurolate dianion **2** with benzylidene chloride and dibromomethane afford benzo-1,3-ditelluroles **3** and **4** in 32 and 58% yields, respectively (Scheme 2).

Scheme 1



1 **2** **3**

Scheme 2



1 **2** **3**

R = Ph (**3**), H (**4**)

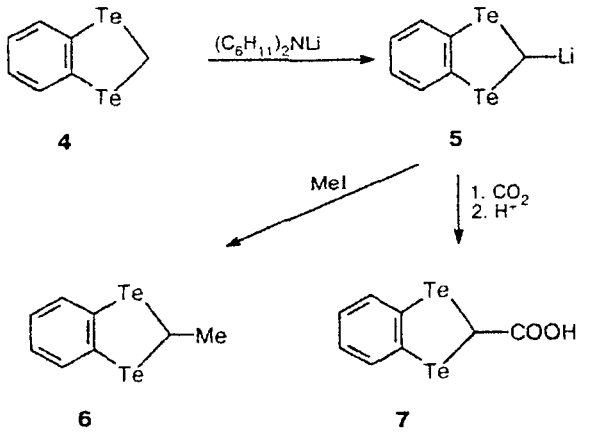
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1132—1134, June, 2000.

1066-5285/00/4906-1127 $25.00

However, we failed to prepare benzo-1,3-ditelluroles containing such electron-withdrawing groups as methoxycarbonyl (from salt **2** and methyl dichloroacetate) and phenylimino (from dianion **2** and phenyl isocyanide dichloride $PhN{=}CCl_2$) at position 2 of the heterocycle, although sulfur and selenium derivatives are easily formed in the reactions of the dichloro derivatives indicated above with the corresponding dichalcogenolate dianions.[1]

We studied metallation of benzo-1,3-ditellurole. Unlike benzo-1,3-dithiole and its 2-R-substituted derivatives, which can be lithiated by butyllithium,[1] the C—Te bonds in benzo-1,3-ditellurole (**4**) as in its noncyclic analogs, diorganyl tellurides R_2Te, are cleaved by butyllithium.[6] As a result, the reaction of heterocycle **4** with BuLi even at low temperatures affords a complex mixture of various diorganyl tellurides. However, 2-lithiobenzo-1,3-ditellurole (**5**) was obtained in a rather low yield by treatment of a solution of heterocycle **4** in THF with lithium dicyclohexylamide. 2-Methylbenzo-1,3-ditellurole (**6**) was obtained in 38% yield by the reaction of lithium derivative **5** with MeI, and carbonization of compound **5** gave benzo-1,3-ditellurole-2-carboxylic acid (**7**) in a yield higher than 27% (Scheme 3).

Scheme 3



Some of the synthesized compounds were tested for biological activity (test for acidic hemolysis of rat erythrocytes[7]). The tests showed that these compounds accelerated acidic hemolysis, and the effect depended on the dose of the compound (within the concentration range of 10^{-5}—10^{-3} mol L^{-1}).

Experimental

IR spectra were recorded on a Specord M-40 spectrometer as suspensions in Nujol. ^1H NMR spectra were recorded on a Tesla BS 487C spectrometer (80 MHz), using HMDS as the internal standard.

Poly(*o*-phenylene ditelluride) (**1**) was synthesized by known procedures.[2,3]

2-Phenylbenzo-1,3-ditellurole (3). A. Dry $NaBH_4$ (1.04 g, 0.03 mol) was added portionwise to a vigorously stirred suspension of compound **1** (5 g, 0.015 mol) in EtOH (80 mL) in an atmosphere of Ar at 60 °C. The reaction mixture was cooled to −15 °C, and a solution of benzylidene chloride (2.4 g, 0.015 mol) in hexane (20 mL) was added over 30 min. The temperature of the mixture was raised to 60 °C, and the mixture was stirred for 30 min at this temperature. Then hexane (70 mL) and water (50 mL) were added, and the mixture was boiled for 10 min with vigorous stirring. After cooling, the hexane layer was separated, washed with water, dried with $MgSO_4$, and concentrated. The precipitate that formed was filtered off and dried. Compound **3** (0.66 g, 15%) was obtained as yellow needles with m.p. 178 °C (from hexane). Found (%): C, 36.98; H, 2.33. $C_{13}H_{10}Te_2$. Calculated (%): C, 37.05; H, 2.37. ^1H NMR ($CDCl_3$), δ: 6.40 (s, 1 H, CH); 7.10—7.35 (m, 9 H, aromatic protons).

B. A 40% solution (5 g) of hydrazine hydrate (0.04 mol) was added dropwise to a suspension of compound **1** (3.32 g, 0.01 mol) and NaOH (1.6 g, 0.04 mol) in DMF (60 mL) in an atmosphere of Ar at 60 °C with vigorous stirring. Warming of the reaction mixture occurred. After stirring for 1 h at 80 °C, the suspension of polyditelluride completely disappeared. The reaction mixture was cooled to −5 °C, and a solution of benzylidene chloride (1.67 g, 0.01 mol) in hexane (10 mL) was added dropwise with stirring. The temperature of the mixture was raised to 80 °C, and the mixture was stirred for 30 min at this temperature. After cooling, the reaction mixture was poured into water and extracted with hexane. Ditellurole **3** (1.32 g, 32%) was isolated from the hexane extract.

2-Methylbenzo-1,3-ditellurole (6). A 1.52 *M* solution (2 mL) of butyllithium in hexane (0.003 mol) was added to a solution of dicyclohexylamine (0.54 g, 0.003 mol) in anhydrous THF (20 mL) at −80 °C with stirring in an atmosphere of Ar. After stirring for 1 h at −80 °C, a solution of compound **4** (1.04 g, 0.003 mol) in THF (20 mL) was added dropwise to the reaction mixture, and the resulting mixture was stirred for 1 h at the same temperature. Then a solution of MeI (0.43 g, 0.003 mol) in anhydrous THF (5 mL) was added to the obtained solution with stirring at −80 °C at such a rate that the temperature of the reaction mixture did not rise above −70 °C. After stirring for 1 h, the temperature of the reaction mixture was slowly raised to 0 °C, and the mixture was poured into water. The product was extracted with hexane. The hexane extract was concentrated in an atmosphere of Ar and cooled to −15 °C, after which heterocycle **6** was isolated as yellow crystals, m.p. 126 °C (from hexane), yield 0.41 g (37.9%). Found (%): C, 26.60; H, 2.24. $C_8H_8Te_2$. Calculated (%): C, 26.75; H, 2.24. ^1H NMR ($CDCl_3$), δ: 2.74 (d, 3 H, Me); 5.00 (q, 1 H, CH); 7.10—7.40 (m, 4 H, Ar).

Benzo-1,3-ditellurole-2-carboxylic acid (7). Solid CO_2 was added to a solution of compound 5 obtained as described above, and the reaction mixture was stirred for 1 h, while the temperature was slowly raised to 0 °C. The reaction mixture was poured into water (100 mL), the precipitate that formed was filtered off, and the aqueous layer was acidified with concentrated HCl to a strongly acidic reaction and extracted with $CHCl_3$. The chloroform solution was washed with water, dried with $MgSO_4$, and evaporated in air. Compound **7** (0.31 g, 26.5%) was obtained as yellow crystals with m.p. 204 °C (from the $CHCl_3$—hexane mixture). Found (%): C, 24.80; H, 1.60. $C_8H_6O_2Te_2$. Calculated (%): C, 24.65; H, 1.55. IR (Nujol), ν/cm^{-1}: 3380 (OH), 2513, 2420, 1700 (CO), 1646, 1580 (Ar), 1300, 1260, 1153, 1113, 1046, 1006, 833, 740, 687, 647.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-3313a).

References

1. I. D. Sadekov, B. B. Rivkin, and V. I. Minkin, *Sulf. Rep.*, 1993, **15**, 10.
2. B. B. Rivkin, I. D. Sadekov, and V. I. Minkin, *Khim. Geterotsikl. Soedin.*, 1988, **8**, 1144 [*Chem. Heterocycl. Compd.*, 1988, **8** (Engl. Transl.)].
3. I. D. Sadekov, B. B. Rivkin, P. I. Gadjieva, and V. I. Minkin, *Heteroatom. Chem.*, 1991, **2**, 307.
4. I. D. Sadekov, B. B. Rivkin, P. I. Gadjieva, and V. I. Minkin, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 387 [*Russ. Chem. Bull.*, 1993, **42**, 350 (Engl. Transl.)].
5. M. Miyashita, M. Hoshino, and A. Yoshikoshi, *Tetrahedron Lett.*, 1988, **29**, 347.
6. N. Petragnani, *Tellurium in Organic Chemistry*, Academic Press, London, 1994, 248 pp.
7. P. I. Gadjieva, A. R. Aliskerov, and N. K. Klichkhanov, *Tez. IV region. konf. "Khimiki Severnogo Kavkaza proizvodstvu" [IV Region Conf. "Chemists of Northern Caucasus for Industry"] (Makhachkala, May 21—24, 1996)*, Makhachkala, 1996, 103 (in Russian).

Received November 13, 1999;
in revised form March 21, 2000