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Synthesis of Benzo-1,3-ditellurole and Its Precursors

I. D. Sadekov, B. B. Rivkin, P. I. Gadjieva, and V. I. Minkin*

Institute of Physical and Organic Chemistry, Rostov University, Rostov-on-Don 344711, U.S.S.R.

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ABSTRACT

Poly(o-phenyleneditelluride) **6** *has been prepared by the reduction of 1,2-bis(trichlorotelluro)benzene obtained by treatment of 1,2-bis(trimethylsilyl)benzene with* $TeCl_4$. *The reduction of* **6** *with* $NaBH_4$ *in ethanol solution affords sodium benzene-1,2-ditellurolate, which, upon treatment with methylene bromide, forms benzo-1,3-ditellurole in 40–47% yield. Benzo-1,3-ditellurole has also been synthesized in 18–20% yield by the reaction of 1,2-bis(trimethylsilyl)benzene with bis(trichlorotelluro)methane, with subsequent reduction of the product, 1,1,3,3-tetrachlorobenzo-1,3-ditellurole.*

INTRODUCTION

Special attention has been paid in the last few years to the development of various methods for the preparation of tetratellurafulvalenes and their derivatives [1–7], which serve as the components of charge-transfer complexes and radical ion salts possessing high electric conductivity and even superconductivity at low temperatures. A general approach to tetratellurafulvalenes involves the reaction of vicinal dilithioethenes with elemental tellurium and subsequent treatment of the dilithium 1,2-ditellurolates formed in this reaction with tetrachloroethene. An essential drawback inherent in this procedure is the formation, along with the target compounds, of substantial amounts of their six-membered ring isomers, 1,4,5,8-tetratelluranaphthalenes [2–5]. It is quite possible that analogous by-products can be formed in the course of the reaction of the lithium salt of benzene-1,2-ditellurol with tetrachloroethene aimed at the synthesis of dibenzotetratellurafulvalene [8]. In this connection, the development of preparative methods based on the precursors already containing five-membered 1,3-ditellurole ring fragments seems necessary. The analogous approach proved to be efficient in the chemistry of sulfur and selenium analogs of tetratellurafulvalenes [9–13]. The synthesis of benzo-1,3-ditellurole described in this paper serves as a step in this direction. A preliminary communication concerning preparation of benzo-1,3-ditellurole has been published elsewhere [14].

RESULTS AND DISCUSSION

Benzo-1,3-ditellurole **1** has been prepared by a four-step synthetic procedure (Scheme 1), the last two steps representing a one-pot reaction, starting from 1,2-bis(trimethylsilyl)benzene **2**. As in the case of the reaction of 1,4-bis(trimethylsilyl)benzene with tellurium tetrachloride, which we have previously studied [15], the substitution of both trimethylsilyl groups by $TeCl_3$-groups occurs only at rather high temperature, that is, upon refluxing an *o*-dichlorobenzene solution of the reactants for 2 h. 1,2-Bis(trichlorotelluro)benzene **3a** has been obtained in 46% yield. By contrast, when using other solvents with lower boiling points (benzene or toluene), the substitution of only one trimethylsilyl group was achieved in this reaction, giving rise to *o*-trimethylsilyl(trichlorotelluro)benzene **4**. A distinctive feature of compound **4**, as compared to other aryl tel-

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*To whom correspondence should be addressed.

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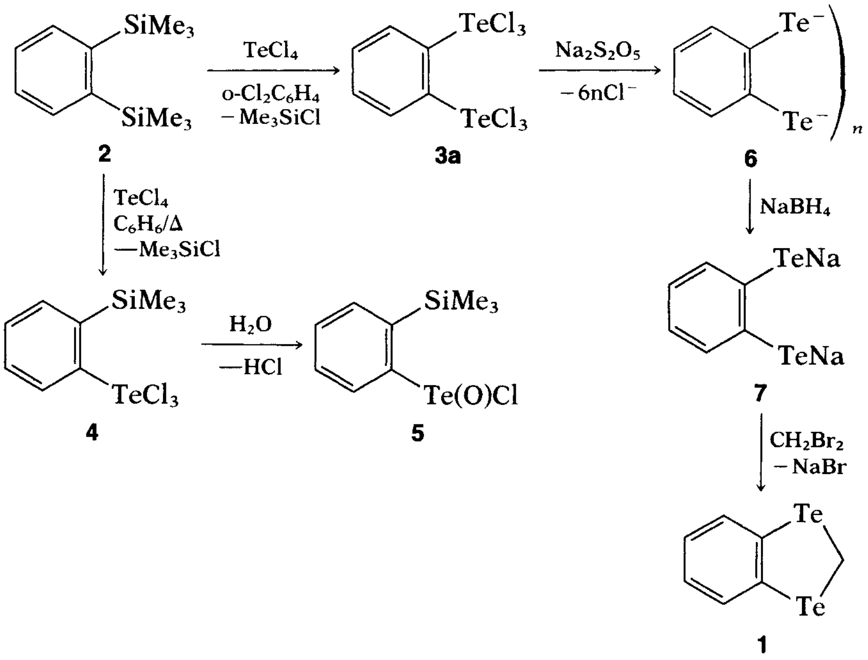


SCHEME 1

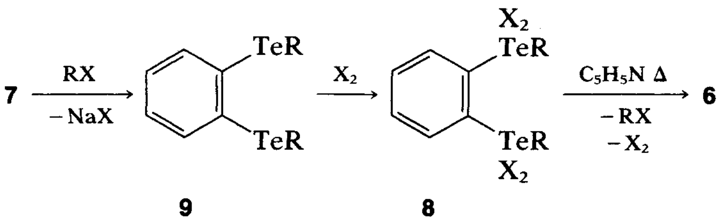
lurium trichlorides, is a fairly good solubility in nonpolar solvents (benzene, hexane). Therefore, this compound was identified in the form of its derivative, *o*-trimethylsilyl phenyltelluroxochloride **5**, to which **4** was converted by hydrolysis at room temperature.

Similarly to other organyl tellurium trichlorides [16,17], compound **3a** is readily reduced with $Na_2S_2O_5$ to the respective ditelluride, poly(*o*-phenyleneditelluride) **6**. Because of the extremely low solubility of **6** in all solvents used, we were unable to determine its molecular weight.

A suspension of **6** in ethanol was reduced by $NaBH_4$ to disodium benzene-1,2-ditellurolate **7**, which was used in situ in the further reaction with dibromomethane, leading to **1** in 40–47% yield. The necessary conditions for this reaction are a sufficiently low temperature (5°C) and concentration (0.03 M). No formation of **1** was observed in the reaction of **7** with dichloromethane, whereas, with diiodomethane, the only product was unidentified insoluble material.

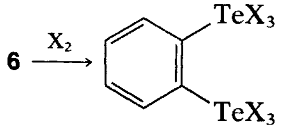
The poly(ditelluride) **6** thus obtained contained as impurity a small amount of elemental tellurium. Samples of **6** free of tellurium were obtained from 1,2-bis(alkyldichloro(or dibromo)telluro)benzenes **8** through refluxing of their pyridine solutions. The latter compounds were prepared in practically quantitative yield by oxidation of 1,2-bis(alkyltelluro)benzenes **9** upon treatment of these with halogens or sulfuryl chloride (Scheme 2). Since tellurides **9** are readily oxidized by atmospheric oxygen, they were isolated in the form of the corresponding tetrahalogeno derivatives **8**.

Similarly to other ditellurides [16, 17], **6** is readily oxidized to 1,2-bis(trihalogenotelluro)benzenes **3a–c** when its suspension in boiling CCl_4 or $CHCl_3$ is treated with halogens (Cl_2, Br_2, I_2) or SO_2Cl_2.



R = a) CH_3, b) C_2H_5, c) n—C_4H_9
X = Cl, Br

SCHEME 2

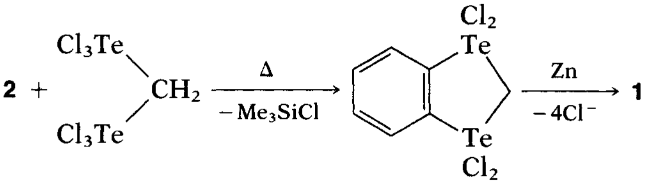


3a–c

X = a) Cl, b) Br, c) I

Benzo-1,3-ditellurole **1** is a light-yellow crystalline (needles) compound readily soluble in most organic solvents. It is easily oxidized when its solutions are exposed to air. The methylene protons of **1** are found in the ^1H NMR spectrum ($CDCl_3$) at δ 4.53. In the UV-spectrum (CH_3CN), three absorption bands are seen at 239, 262, and 310 (shoulder) nm. These data are to be compared with those of benzo-1,3-dithiole [18]: ^1H NMR (CCl_4): δ 4.27, UV (dioxane): 275, 300 nm.

The formation of **1** from **2** can also be effected by first treating **2** with bis(trichlorotelluro)methane, which is readily obtained from acetic anhydride and $TeCl_4$ [19]. By heating an *o*-dichlorobenzene solution of these reagents, 1,1,3,3-tetrachlorobenzo-1,3-ditellurole **10** is formed, which, similarly to other tetracoordinate tellurium derivatives [17], can be readily reduced, affording **1**. The total yield of **1** obtained by this procedure is 18–20%.



10

Since **6** serves as a good precursor in the synthesis of **1**, we studied alternative approaches to **6**. It was known that the selenium analog of **1** was obtained in comparatively low yield (26%) by treatment of dibromobenzene with Na_2Se_2 in DMF [20]. However, in our attempt to react *o*-diiodbenzene with Na_2Te_2 in HMPTA, the only isolable tellurium-containing compound happened unexpectedly to be telluranthrene, which was obtained in 12% yield [21].

Because of the insolubility of the poly(ditelluride) **6**, the attempts to obtain **1** through the insertion of methylene (generated from diazomethane) or dichlorocarbene (from CCl_3COONa) into the Te—Te bond of **6** failed. At the same time, aromatic ditellurides are prone to such reactions affording, upon treatment with diazomethane, bis(aryltelluro)-methanes in high yield [22].

EXPERIMENTAL

^1H NMR spectra were recorded on a Tesla-BS487C (80 MHz) instrument, using HMDS as internal standard in $CDCl_3$, CCl_4, or DMSO-d_6 solutions. UV spectra were recorded on a Specord-M-40 spectrometer in CH_3CN.

1,2-Bis(trimethylsilyl)benzene (2)

To a suspension of 2.92 g (120 mmol) of Mg shavings activated with a small amount of I_2, 7.35 g (50 mmol) of *o*-dichlorobenzene and 11.95 g (110 mmol) of trimethylsilyl chloride were added, with stirring. The reaction mixture was heated in a boiling water bath for 40 h, cooled, and then extracted with heptane (3 × 20 mL). The heptane solution was washed with water and dried ($MgSO_4$), and the solvent was evaporated in vacuum. Subsequent distillation in vacuum affords 6.5 g (58%) of **2** as a colorless liquid, bp 110–115°C/5 torr.

1,2-Bis(trichlorotelluro)benzene (3a)

a) From **2** and $TeCl_4$: In a three-necked flask equipped with a mechanical stirrer and reflux condenser, a mixture of 8.1 g (30 mmol) $TeCl_4$ and 3.34 g (15 mmol) of **2** was refluxed for 2 h. After cooling, the precipitate that had formed was filtered off, washed with ether, and dried to give 3.8 g (46%) of **3a** as colorless crystals, mp 292–294°C (from toluene). Analysis, calculated for $C_6H_4Cl_6Te_2$, C, 13.24; H, 0.74; found, C, 12.96; H, 0.91.

b) From **6** and Cl_2: A stream of dry chlorine was passed through the stirred boiling suspension of 3.32 g (10 mmol) of **6** in 60 mL of $CHCl_3$ for 40 min. The reddish-brown color of poly(ditelluride) disappeared. Then the mixture was cooled, the precipitate was filtered off, washed with $CHCl_3$, and dried to give 5.16 g (95%) of **3a** as colorless crystals, mp 294°C (from toluene).

2-(o-Trimethylsilyl)phenyltelluroxochloride (5)

A solution of 6.1 g (22.5 mmol) of $TeCl_4$ and 5.0 g (22.5 mmol) of **2** in 50 mL of toluene was refluxed for 1.5 h. The solvent was removed in vacuo, and the residual oil was extracted twice with 30 mL of boiling hexane. This extract was shaken with 20 mL of water. The precipitate that formed was filtered off, washed with water, and dried to give 4.52 g (61%) of **5** as white crystals, mp 201–203°C (from $CHCl_3$-hexane). Analysis, calculated for $C_9H_{13}OSiClTe$, C, 32.92; H, 3.99; found C, 34.05; H, 4.28.

Poly(o-phenyleneditelluride) (6)

a) From **3a**: 16.33 g (30 mmol) of **3a** was added in small portions to a vigorously stirred 20% water solution of $Na_2S_2O_5$ (100 mL) at 60–80°C for 10 min. After cooling the precipitate of poly(ditelluride) was collected, washed with some portions of water, and dried. The yield is quantitative. The reddish-brown precipitate had no well-defined mp. Analysis, calculated for $C_6H_4Te_2$, C, 21.75; H, 1.21; found, C, 20.85; H, 0.96.

b) From **8**: A solution of 10 mmol of **8** and 3.16 g (40 mmol) of pyridine in 30 mL of dioxane was refluxed for 2–4 h. The mixture was cooled. The precipitate of **6** was collected by filtration, washed with hot water, and dried. Yield is 61–90%. The material melted over the interval of 143–158°C.

Benzo-1,3-ditellurole (**1**)

A solution of 1 g (26 mmol) of $NaBH_4$ in 10 mL of a 2.5 N aqueous solution of NaOH was added dropwise to a vigorously stirred suspension of 5 g (15 mmol) of **6** in 1 L of boiling ethanol under argon. The mixture was heated at reflux with stirring for 5 min, then quickly cooled to 5°C, and a solution of 2.5 g (15 mmol) of dibromomethane in 5 mL of ethanol was added over 30 min. It was heated at reflux with stirring for 10 min, then concentrated under argon to a volume of 100 mL. Following this, 70 mL of hexane and 100 mL of 5% aq HCl were added, and the mixture was heated at reflux for 10 min. The hexane extract of the ditellurole was separated and cooled to -10°C. The resulting precipitate, 2.43 g, (47%) of **1** was filtered off and dried in vacuum-desiccator. Yellow crystals were recrystallized from hexane, mp 98°C; 80-MHz ^1H NMR ($CDCl_3$), δ 4.53 (s, 2H, —CH_2—), 6.80–7.30 (m, 4H, aromatic protons). Analysis, calculated for $C_7H_6Te_2$, C, 24.35; H, 1.78; found, C, 24.56; H, 1.99.

Benzo-1,3-ditellurole (**1**) *from* **2** *and bis(trichlorotelluro)methane*

A mixture of 7.23 g (15 mmol) of bis(trichlorotelluro)methane and 4.2 g (19 mmol) of **2** in 10 mL of *o*-dichlorobenzene was refluxed with stirring for 0.5 h. After cooling, **10** was filtered off (4 g), washed with ether, and dried. The reduction of 4 g of this compound, **10**, with zinc dust in isopropyl alcohol by the usual method [17] followed by extraction of the residue and removal of the solvent gave 1 g of pure **1** (19.4%).

1,2-Bis(methyltelluro)benzene (**9a**)

A solution of 0.99 g (26 mmol) of $NaBH_4$ in 10 mL of a 2.5 N aqueous solution of NaOH was added dropwise to a vigorously stirred suspension of 4.25 g (12.8 mmol) of **6** in 350 mL of boiling ethanol under argon. After 5 min of refluxing, the solution was cooled to room temperature, and a solution of 3.23 g (26 mmol) of dimethyl sulphate in 5 mL of ethanol was added dropwise and refluxed for 1 h. About $\frac{2}{3}$ of the solvent was removed by rotary evaporation, and 70 mL hexane and 50 mL of water were added to the residue. The mixture was then refluxed for 5 min. After cooling, the hexane layer was separated, washed with water and concentrated under argon. After keeping the solution at -10°C, the precipitate that had formed was filtered off and dried to give 3.33 g (72%) of light-yellow crystals, mp 46–47°C (from pentane); 80-MHz ^1H NMR ($CDCl_3$), δ 2.12 (s, 6H, CH_3), 7.04–7.49 (m, 4H, aromatic protons). Analysis, calculated for $C_8H_{10}Te_2$, C, 26.59; H, 2.79; found, C, 26.67; H, 2.91.

1,2-Bis(methyldichlorotelluro)benzene (**8a**^{1}) (*X = Cl*)

A stream of dry chlorine was passed through the stirred boiling solution of 1.81 g (5 mmol) of compound **9a** in 15 mL of CCl_4. The mixture was cooled after 15–20 min of stirring. The precipitated solid was filtered off, washed with ether, and dried to give 2.31 g (92%) of colorless solid, mp 200°C (from dioxane-hexane); 80-MHz ^1H NMR (DMSO-d_6), δ 3.00 (s, 6H, CH_3), 7.44–8.73 (m, 4H, aromatic protons). Analysis, calculated for $C_8H_{10}Cl_4Te_2$, C, 19.09; H, 2.00; found, C, 19.25; H, 1.85.

1,2-Bis(methyldibromotelluro)benzene (**8a**^{2}) (*X = Br*)

A solution of 1.81 g (5 mmol) of compound **9a** and 1.6 g (10 mmol) of bromine in 15 mL $CHCl_3$ was refluxed for 30 min. The mixture was cooled, the solid that had formed was filtered off, washed with ether, and dried to give 3.27 g (96%) yellow solid, mp 208°C (from dioxane-hexane). Analysis, calculated for $C_8H_{10}Br_4Te_2$, C, 14.11; H, 1.48; found, C, 14.29; H, 1.37.

1,2-Bis(alkyldihalogenotelluro)benzenes (**8**) (*R = C_2H_5, n-C_4H_9, X = Cl, Br*)

The preparation of **9b** or **9c** was analogous to the synthesis of **9a** with the exception of the final stage, when 25.6 mmol of RBr (R = C_2H_5, *n*-C_4H_9) was added dropwise to the stirred solution following the reduction and refluxed for 30 min. Two thirds of the solvent was removed, 70 mL hexane and 50 mL of water were added, and the mixture was refluxed for 5 min. After cooling the hexane layer was separated, washed with water, dried over anhydrous Na_2SO_4, and concentrated under argon to a volume of 20 mL. The residue was mixed with 40 mL of freshly distilled $CHCl_3$ and the resulting solution was divided into two halves. Each half was then treated with the corresponding halogen.

A stream of dry chlorine was passed through one half of this solution with vigorous stirring and refluxing for 10 min. After cooling, the resulting precipitate was filtered off, washed with CCl_4, and dried to give 83% of colorless solid of 1,2-bis(ethyldichlorotelluro)benzene (**8b**^{1}), mp 184°C (from dioxane-hexane). Analysis, calculated for $C_{10}H_{14}Cl_4Te_2$, C, 22.60; H, 2.65; found, C, 22.54; H, 2.95.

1,2-Bis(butyldichlorotelluro)benzene (**8c**[1])

This compound was obtained in 89% yield. Colorless solid, mp 173°C (from dioxane-hexane). Analysis, calculated for $C_{14}H_{22}Cl_4Te_2$, C, 28.62; H, 3.78; found, C, 28.32; H, 3.63.

To the other half of the solution, upon vigorous stirring and refluxing, a solution of 3.0 g bromine in 15 mL $CHCl_3$ was added dropwise until the appearance of a stable bromine color. The precipitate that formed was filtered off, washed with CCl_4, and dried; 1,2-Bis(ethyldibromotelluro)benzene (**8b**[2]), was obtained in 79% yield. Yellow crystals, mp 168°C (from dioxane-hexane). Analysis, calculated for $C_{10}H_{14}Br_4Te_2$, C, 16.94; H, 1.99; found, C, 16.45; H, 1.86.

1,2-Bis(butyldibromotelluro)benzene (**8c**[2])

This compound was obtained in 84% yield. Yellow crystals, mp 166°C (from dioxane-hexane). Analysis, calculated for $C_{14}H_{22}Br_4Te_2$, C, 21.98; H, 2.90; found, C, 21.88; H, 2.60.

1,2-Bis(tribromotelluro)benzene (**3b**)

A suspension of 1.0 g (3.0 mmol) of poly(*o*-phenyleneditelluride) **6** and 5.0 g (excess) of bromine in 40 mL of $CHCl_3$ was refluxed with stirring for 50 min. The mixture was cooled, the precipitate that formed was filtered off, washed with $CHCl_3$, and dried to give 2.42 g (approximately 100%) of bright-yellow crystals, mp 318°C. Analysis, calculated for $C_6H_4Br_6Te_2$, C, 8.89; H, 0.49; found, C, 8.50; H, 0.52.

1,2-Bis(triiodotelluro)benzene (**3c**)

A suspension of 1.0 g (3.0 mmol) **6** and 2.54 g (10 mmol) of iodine in 60 mL of toluene was refluxed for 2 h. The mixture was cooled, washed with toluene, and dried. Black-violet crystals, 3.24 g (98%) yield, mp 192°C were obtained. Analysis, calculated for $C_6H_4I_6Te_2$, C, 6.61; H, 0.37; found, C, 6.72; H, 0.43.

REFERENCES

[1] F. Wudl, E. Aharon-Shalom, *J. Am. Chem. Soc., 104,* 1982, 1154.

[2] N. Okada, G. Saito, T. Mori, *Chem. Letters,* 1986, 311.

[3] N. Okada, G. Saito, T. Mori, *Synt. Metals, 19,* 1987, 589.

[4] R. D. McCullough, G. B. Kok, K. A. Lerstrup, D. O. Cowan, *J. Am. Chem. Soc., 109,* 1987, 4115.

[5] K. A. Lerstrup, A. Bailey, R. D. McCullough, M. Mays, D. O. Cowan, *Synt. Metals, 19,* 1987, 647.

[6] K. A. Lerstrup, M. Lee, D. O. Cowan, T. Kistenmacher, *Mol. Cryst. Liq. Cryst., 120,* 1985, 295.

[7] K. A. Lerstrup, D. O. Cowan, T. Kistenmacher, *J. Am. Chem. Soc., 106,* 1984, 8303.

[8] K. A. Lerstrup, D. Talham, A. Bloch, T. Poehler, D. O. Cowan, *J. Chem. Soc., Chem. Comm.,* 1982, 336.

[9] N. Lozach, M. Stavaux, *Advances in Heterocyclic Chemistry,* 27, 1980, 151.

[10] M. R. Bryce, *Annu. Repts. Progr. Chem., C82,* 1985, 377.

[11] V. Yu. Hodorkovskii, O. Ia. Neyland, *Izv. Akad. Nauk Latv. SSR, Ser. khim.,* 1985, 645.

[12] A. Krief, *Tetrahedron, 42,* 1986, 1209.

[13] G. Schukat, A. M. Richter, E. Fanghanel, *Sulfur Reports,* 7, 1987, 155.

[14] B. B. Rivkin, I. D. Sadekov, V. I. Minkin, *Khim. Geterotsikl. Soed.,* 1987, 1144.

[15] I. D. Sadekov, B. B. Rivkin, A. A. Maksimenko, V. I. Minkin, *Zh. Obshch. Khim., 57,* 1987, 1559.

[16] K. J. Irgolic: *The organic chemistry of tellurium,* Gordon and Breach, New York, 1974.

[17] I. D. Sadekov, A. A. Maksimenko, V. I. Minkin: *The chemistry of tellurium-organic compounds,* Rostov University Press, Rostov, U.S.S.R., 1983.

[18] D. Seebach, K. H. Geib, A. K. Beck, B. Graf, H. Daum, *Chem. Ber., 105,* 1972, 3280.

[19] C. W. Dirk, D. Nalewayek, G. B. Blanchet, H. Schaffer, F. Moraes, R. M. Boysel, F. Wudl, *J. Am. Chem. Soc., 107,* 1985, 675.

[20] D. J. Sandman, G. W. Allen, L. A. Acampora, J. C. Stark, S. Jansen, M. T. Jones, G. J. Ashwell, B. M. Foxman, *Inorg. Chem., 26,* 1987, 1664.

[21] B. B. Rivkin, I. D. Sadekov, P. I. Gadjieva, V. I. Minkin, *Khim. Geterotsikl. Soed.,* 1990, 137.

[22] N. Petragnani, H. Schill, *Chem. Ber., 103,* 1970, 2271.