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3*H*(3R)-Benzo-2,1-oxatelluroles as Synthons in Synthesis of *o*-Alkyltellurophenyl Carbonyl Compounds

Igor D. Sadekov, Alexander A. Maksimenko and Vladimir I. Minkin*

Laboratory of Tellurium Chemistry, Institute of Physical and Organic Chemistry,
Rostov State University, Rostov on Don 344104, Russia

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Abstract: *A covenient method, developed for the preparation of o-alkyltelluro-benzaldehydes and -phenyl-ketones from o-alkyltellurobenzyl alcohols, involves the intermediate formation and rearrangement of 3H(3R)-benzo-2,1-oxatelluroles, a novel tellurium-containing heterocyclic system .*

INTRODUCTION

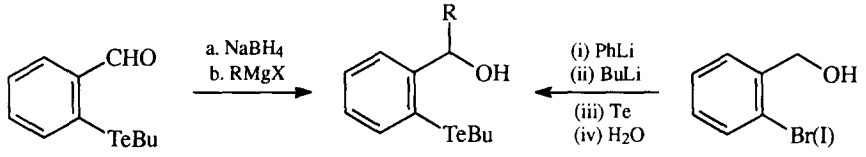
The characteristic reactivity of organotellurium compounds, especially the facile heterolysis of C-Te bond and the tendency of Te(II) derivatives to undergo oxidative addition, results in the simultaneous modification or even expulsion of a tellurium-containing substituents under the conditions of various transformations of organic functionalities[1]. For this reason, attempts to obtain *o*-methyltellurobenzaldehyde[2] or *o*-methyltelluroacetophenone[3] failed using methods commonly employed in the chemistry of carbonyl compounds, e.g. by oxidation of the C-methyl group of *o*-methylphenyl methyl telluride with various oxidants, or by oxidation of *o*-(1′-hydroxyethyl)phenyl methyl telluride with DMSO in acetic anhydride. In both these cases, cleavage of the C-Te bonds readily occurred to give TeO_2. Aromatic aldehydes[2] and ketones[3,4], containing an *o*-alkyltelluro substituent, have been obtained by insertion of Te into the C-Li bonds of the correspondingly protected *o*-lithiobenzaldehyde[2], *o*-lithioacetophenone[3] or *o*-lithiobenzophenone[4] followed by alkylation of the lithium tellurophenolates formed. Another route to *o*-methyltellurobenzophenone involves the

reactions of 2-chlorocarbonylphenyl methyl telluride with diphenylcadmium, or 2-chlorotellurenylbenzophenone with dimethylcadmium[5]. *o*-Phenyltellurobenzophenone has also been prepared by the $S_{RN}1$ reaction of *o*-bromobenzophenone with phenyltellurolate anion generated by electrochemical reduction of diphenyl ditelluride[6].

We now report the development of a new and convenient method for the synthesis of *o*-alkyltellurobenzaldehydes and ketones from *o*-alkyltellurobenzyl alcohols involving the intermediate formation and rearrangement of a tellurium-containing heterocyclic system: 3*H*(3R)-benzo-2,1-oxatellurole.

RESULTS AND DISCUSSION

1-Halogeno-1-butyl-3*H*-benzo-2,1-oxatelluroles **1** were obtained in high yields by dehydrohalogenation of 2-butyldihalogenotellurobenzyl alcohols **2a-d** or their derivatives **2e-n** (Table 1). Compounds **2a-n** were prepared by oxidation of the corresponding benzyl alcohols **3a-d** with halogens. The alcohols **3a-d** were synthesized from 2-butyltellurobenzaldehyde in 70-90% yields: **3a** by reduction with $NaBH_4$, and **3b-d** by coupling with the Grignard reagents[7,8]. The alternative approach to 2-butyltellurobenzyl alcohol **3a** included the reaction of 2-bromo- or 2-iodobenzyl alcohols with phenyllithium followed by the subsequent treatment of the lithium alcoholates thus formed with butyllithium and powdered tellurium[8]. The yields of **3a** were 55% and 60% respectively.

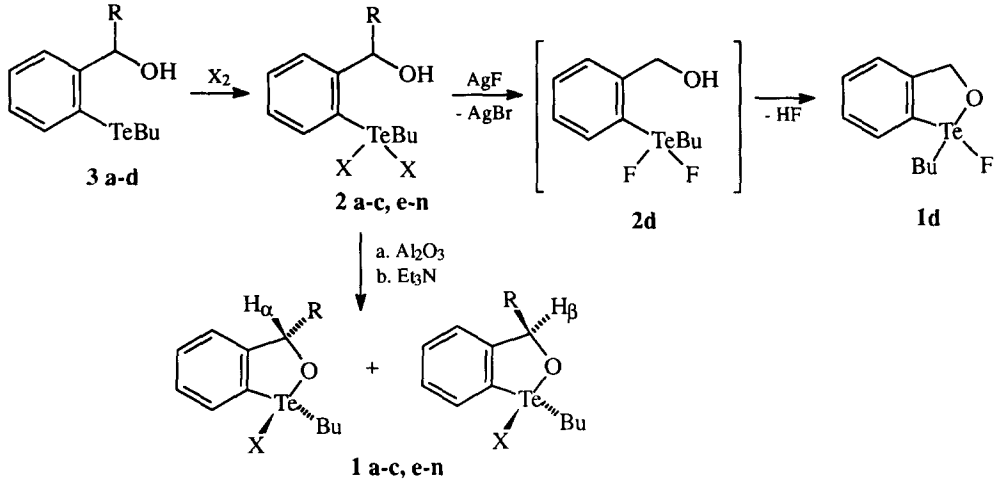


3 a-d

3 a R = H; **b** R = Ph; **c** R = 4-MeC_6H_4; **d** R = Me

The terms of dehydrogalogenation of benzyl alcohols **2a-n** with formation of the heterocycles **1a-n** are determined by the nature of a halogen atom at the tellurium center. Thus, 2-butyldifluorotellurobenzyl alcohol **2d**, obtained from 2-butyldibromotellurobenzyl alcohol **2b** by the exchange reaction with silver(I) fluoride, underwent spontaneous cyclization into 1-butyl-1-fluoro-3*H*-benzo-2,1-oxatellurole **1d** in 87% yield. The 1-chloro-substituted derivative **1a** was formed, if a chloroform solution of 2-butyl-dichlorotellurobenzyl alcohol **2a** was passed through a column filled with aluminum oxide, or on treatment with the equimolar amount of

triethylamine. A treatment with triethylamine was also a necessary step in cyclization of dibromo and diiodo derivatives **2b,c**.

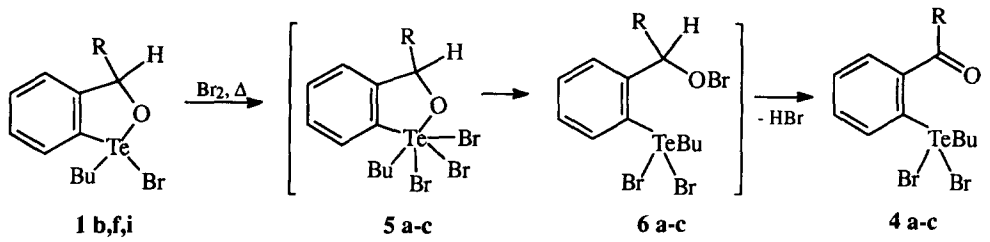


3 a-d **2 a-c, e-n** **2d** **1d** **1 a-c, e-n**

1,2 **a** R = H, X = Cl; **b** R = H, X = Br; **c** R = H, X = I; **e** R = Ph, X = Cl; **f** R = Ph, X = Br; **g** R = Ph, X = I; **h** R = 4-MeC_6H_4, X = Cl; **i** R = 4-MeC_6H_4, X = Br; **k** R = 4-MeC_6H_4, X = I; **l** R = Me, X = Cl; **m** R = Me, X = Br; **n** R = Me, X = I

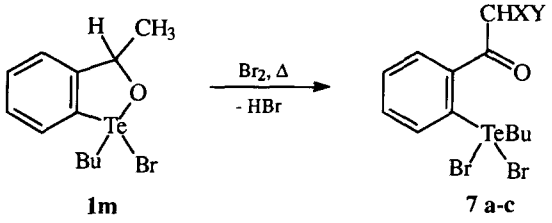
The cyclization of the secondary benzyl alcohols **2e-n** led to the formation of mixtures of two diastereoisomers identified by the ^1H NMR spectral data. Thus, for the methyl-substituted oxatellurole **1m**, the methine proton appeared for two isomers as two quartets at δ 5.48 and 5.75, and for the phenyl-substituted oxatellurole **1f**, as two singlets at δ 6.28 and 6.57. In both these cases, the ratio of diastereoisomers was about 1:1, whereas in other mixtures one of the diastereoisomers was predominant. The bias in the diastereomeric mixtures **1e-n** increased with increase in the mass of the halogen atom at the tellurium center. Thus, for 4′-methylphenyl-substituted oxatelluroles **1h,i** and **k**, the ratio of diastereoisomers was 1:2, 1:2.5 and 1:3, respectively. The characteristics of oxatelluroles **1** are presented in Table 2.

We found that interaction of 1-bromo derivatives **1b,f,i** with bromine resulted in the rupture of the O-Te bonds with the formation of aldehyde **4a** (from **1b**) or ketones **4b,c** (from **1f,i**) which all contain a tellurium functionality -Te(Bu)Br_2 in the *ortho*-position. The compounds **4a-c** were obtained in 95%, 78% and 73% yields respectively, if the equimolar amounts of bromo derivatives **1b,f,i** and bromine were refluxed in chloroform or in carbon tetrachloride[7,8]. Probably, the mechanism of this reaction includes the intermediate formation of hexacoordinated tellurium derivatives **5** followed by rearrangement to hypobromites **6** and subsequent elimination of HBr.



1 b,f,i **5 a-c** **6 a-c** **4 a-c**

4-6 **a** R = H; **b** R = Ph; **c** R = 4-MeC_6H_4

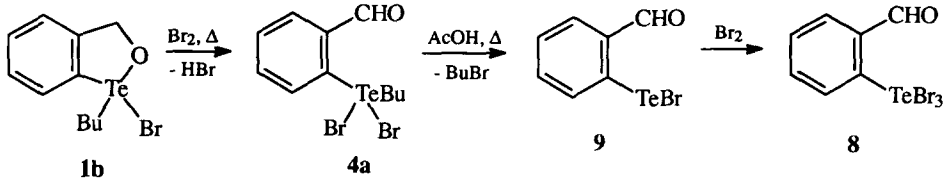


1m **7 a-c**

7 **a** X = Y = H; **b** X = H, Y = Br; **c** X = Y = Br

We expected that the coupling reaction of 3-methyl-substituted benzoxatellurole **1m** with an equimolar amount of bromine would lead to dibromotelluroacetophenone **7a**, which could eliminate butyl bromide to give 2-bromotellurenylacetophenone, a precusor in the synthesis of telluroindoxyl[9]. However, the reaction was accompanied by bromination at the methyl group, and the resulting mixture contained ω-bromoacetophenone **7b** as the major product. The use of a two-fold molar amount of bromine gave a mixture of **7b** and ω,ω-dibromoacetophenone **7c**. The pure compound **7c** was isolated by several successive crystallizations (see Experimental).

The interaction of one mole of benzotellurole **1b** with two moles of bromine on reflux in acetic acid gave rise to 2-tribromobenzaldehyde **8** in 63% yield. A possible mechanism of this transformation implies the formation of **4a** followed by elimination of butyl bromide to give aldehyde **9** which is oxidized by bromine into tribromoaldehyde **8**. The mechanism suggested is supported by isolation of bromoaldehyde **9** in high yield on heating 2-butyldibromotellurobenzaldehyde **4a** in acetic acid in the presence of catalytic amount of HBr.



1b **4a** **9** **8**

Table1. Characteristics of Alcohols **2 b-n**.

Compd	Mp (°C)	^{1}H NMR, δ, ppm	Molecular formula	Found (requires), % C	H	Yield, %
2b	94-96	2.37 (m, C_4H_9), 3.15 (s, OH), 5.04 (s, CH_2), 7.55 (m, C_6H_4)	$C_{11}H_{16}Br_2OTe$	29.10 (29.25)	3.42 (3.57)	83
2c	108-110	2.19 (m, C_4H_9), 2.67 (s, OH), 4.91 (s, CH_2), 7.42 (m, C_6H_4)	$C_{11}H_{16}I_2OTe$	24.31 (24.17)	2.83 (2.95)	60
2e	137-139	2.48 (m, C_4H_9), 3.45 (s, OH), 6.42 (s, CH_2), 7.68 (m, Ph and C_6H_4)	$C_{17}H_{20}Cl_2OTe$	46.38 (46.53)	4.41 (4.59)	64
2f	143-145	2.40 (m, C_4H_9), 3.39 (s, OH), 6.37 (s, CH_2), 7.48 (m, Ph and C_6H_4)	$C_{17}H_{20}Br_2OTe$	38.58(38.70)	3.75(3.82)	77
2g	119-122	2.26 (m, C_4H_9), 3.28 (s, OH), 6.21 (s, CH_2), 7.38 (m, Ph and C_6H_4)	$C_{17}H_{20}I_2OTe$	33.01(32.84)	3.15(3.24)	66
2h	128-129	-	$C_{18}H_{22}Cl_2OTe$	47.68(47.74)	4.66(4.90)	63
2i	135-137	2.10 (m, C_4H_9), 2.32, 2.34 (two s, CH_3), 6.29, 6.70 (two s, CH), 7.48 (m, two C_6H_4)	$C_{18}H_{22}Br_2OTe$	39.69(39.91)	4.20(4.09)	86
2k	118-119	-	$C_{18}H_{22}I_2OTe$	33.92(34.00)	3.55(3.49)	54
2l	92-94	2.45 (m, C_4H_9), 1.75 (d, CH_3, J=6.9 Hz), 3.50 (s, OH), 5.46 (q, CH, J=6.9 Hz), 7.68 (m, C_6H_4)	$C_{12}H_{18}Cl_2OTe$	38.25(38.07)	4.77(4.82)	65
2m	102-105	2.35 (m, C_4H_9), 1.66 (d, CH_3, J=6.8 Hz), 3.13 (s, OH), 5.38 (q, CH, J=6.8 Hz), 7.63 (m, C_6H_4)	$C_{12}H_{18}Br_2OTe$	31.04(30.95)	4.25(3.90)	72
2n	112-115	2.18 (m, C_4H_9), 1.50 (d, CH_3, J=6.8 Hz), 3.05 (s, OH), 5.20 (q, CH, J=6.8 Hz), 7.50 (m, C_6H_4)	$C_{12}H_{18}I_2OTe$	26.00(25.75)	3.18(3.24)	70

Table 2. Characteristics of Benzoxatelluroles **1a-n**.

Compd	Mp (°C)	^{1}H NMR, δ, ppm	Molecular formula	Found (requires), % C	H	Yield, %
1a	114-115	1.79 (m, C_4H_9), 5.32 (d, 1H, CH_2, *J*= 14.4 Hz), 5.32 (d, 1H, CH_2, *J*= 14.4 Hz), 7.68 (m, C_6H_4)	$C_{11}H_{15}ClOTe$	40.29 (40.49)	4.70 (4.63)	89
1b	113-114	1.96 (m, C_4H_9), 5.27 (d, 1H, CH_2, *J*= 14.8 Hz), 5.55 (d, 1H, CH_2, *J*= 14.8 Hz), 7.80 (m, C_6H_4)	$C_{11}H_{15}BrOTe$	35.45 (35.64)	3.99 (4.08)	78
1c	110-112	2.19 (m, C_4H_9), 5.31 (d, 1H, CH_2, *J*= 15.0 Hz), 5.61 (d, 1H, CH_2, *J*= 15.0 Hz), 7.72 (m, C_6H_4)	$C_{11}H_{15}IOTe$	31.35 (31.63)	3.51 (3.62)	75
1d	oil	1.83 (m, C_4H_9), 5.46 (dd, *J*= 15.2 Hz, 3-H), 7.80 (m, C_6H_4)	$C_{11}H_{15}FOTe$	42.35 (42.64)	4.65 (4.88)	85
1e	127-128	2.27 (m, C_4H_9), 6.40, 6.71 (two s, 3-H$_\alpha$ and 3-H$_\beta$), 7.91 (m, Ph and C_6H_4)	$C_{17}H_{19}BrOTe$	51.02(50.74)	4.55(4.76)	70
1f	138-139	2.11 (m, C_4H_9), 6.28, 6.57 (two s, 3-H$_\alpha$ and 3-H$_\beta$), 7.75 (m, Ph and C_6H_4)	$C_{17}H_{19}BrOTe$	45.35(45.69)	4.56(4.29)	82
1g	140-142	1.99 (m, C_4H_9), 6.17, 6.42 (two s, 3-H$_\alpha$ and 3-H$_\beta$), 7.00 (m, Ph and C_6H_4)	$C_{17}H_{19}IOTe$	41.10(41.35)	3.24(3.88)	86
1h	140-141	2.22 (m, C_4H_9), 2.42 (s, CH_3), 6.38, 6.78 (two s, 3-H$_\alpha$ and 3-H$_\beta$), 7.87 (m, two C_6H_4)	$C_{18}H_{21}ClOTe$	51.73(51.95)	5.15(5.08)	79
1i	138-140	2.05 (m, C_4H_9), 2.33 (s, CH_3), 6.29, 6.70 (two s, 3-H$_\alpha$ and 3-H$_\beta$), 7.78 (m, two C_6H_4)	$C_{18}H_{21}BrOTe$	47.17(46.91)	4.65(4.59)	84
1k	100-102	1.98 (m, C_4H_9), 2.26 (s, CH_3), 6.10, 6.65 (two s, 3-H$_\alpha$ and 3-H$_\beta$), 7.60 (m, two C_6H_4)	$C_{18}H_{21}IOTe$	42.50(42.57)	3.89(4.17)	62
1l	124-125	2.12 (m, C_4H_9), 1.52 (d, CH_3, *J*= 6.1 Hz), 5.64, 5.92 (two q, 3-H$_\alpha$ and 3-H$_\beta$, *J*= 6.1 Hz), 7.97 (m, C_6H_4)	$C_{12}H_{17}ClOTe$	42.48(42.35)	5.21(5.04)	81
1m	116-118	2.01 (m, C_4H_9), 1.47 (d, CH_3, *J*= 6.0 Hz), 5.48, 5.75 (two q, 3-H$_\alpha$ and 3-H$_\beta$, *J*= 6.0 Hz), 7.84 (m, C_6H_4)	$C_{12}H_{17}BrOTe$	37.14(37.46)	4.30(4.45)	85
1n	120-121	-	$C_{12}H_{17}IOTe$	33.21(33.38)	4.19(3.97)	62

In conclusion, a novel synthesis of *o*-alkyltellurophenyl carbonyl compounds from *o*-alkyltellurobenzyl alcohols via a new heterocyclic system, 3*H*(3R)-benzo-2,1-telluroles, was developed. The rearrangement of 3*H*(3R)-benzo-2,1-telluroles in reaction with bromine was investigated.

EXPERIMENTAL PART

Melting points were determined on a Yanaco micro m.p. apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) using $CDCl_3$, CD_2Cl_2 or DMSO-d_6 as solvent and tetramethylsilane as internal reference. The solvents used were dried and distilled in accordance with the standard procedures. 2-Butyltellurobanzaldehyde was prepared according to the literature procedure[2].

2-Butyltellurobenzyl alcohol (3a).

Method A. To a solution of phenyllithium, obtained from bromobenzene (8.64 g, 55 mmol) and lithium (1.46 g, 210 mmol) in diethyl ether (50 mL) under argon, a solution of *o*-bromobenzyl alcohol (9.35 g, 50 mmol) in THF (10 mL) was added dropwise under stirring at 10-15^{o}C. To the resulting solution of lithium *o*-bromobenzylate containing unreacted lithium, butyl bromide (6.85 g, 50 mmol) was added dropwise under stirring at 0^{o}C. The mixture was stirred at 8-10^{o}C until the whole amount of lithium reacted (30-40 min). Powdered tellurium (6.38 g, 50 mmol) was added in small portions while the mixture spontaneously boiled and tellurium dissolved. The mixture was refluxed for 1 h, cooled and poured onto ice (100 g). The ether layer was separated, dried ($CaCl_2$), and the solvent removed under vacuum. The residue was distilled *in vacuo* (175-8^{o}C/2 mm Hg) to give **3a** as a pale yellow oil in 85% yield. ^{1}H NMR spectrum, δ ($CDCl_3$): 1.87 (m, 9H, C_4H_9), 3.02 (s, 1H, OH), 4.64 (s, 2H, $C\underline{H}_2OH$), 7.64 (m, 4H, C_6H_4). Found: C, 45.04; H, 5.41. $C_{11}H_{16}OTe$ requires: C, 45.27; H, 5.53.

Method B. To a mixture of *o*-butyltellurobenzaldehyde (5.0 g, 17.3 mmol), ethanol (10 mL) and benzene (5mL), a solution of $NaBH_4$ (0.76 g, 20 mmol) and NaOH (0.8 g, 20 mmol) in water (4 mL) was added dropwise at room temperature under stirring for 1 h. The mixture was poured into water (30 mL) and acidified with 37% aqueous solution HCl to pH 6.0-6.5. The organic layer was separated, washed with water (10 mL x 2) and dried (Na_2SO_4). The solvent was removed under vacuum, and the residue distilled *in vacuo* to give **3a** (4.6 g, 91%).

Phenyl(2-butyltellurophenyl)methanol (3b) and **4-methylphenyl(2-butyltellurophenyl)methanol (3c)** were obtained as solutions in ether from 2-butyltellurobenzaldehyde and phenyl- or 4-methylphenyl-magnesium bromides, respectively and used without isolation for further oxidation into alcohols **2e-l**.

1-(2-Butyltellurophenyl)ethanol (3d) was synthesized from 2-butyltellurobenzaldehyde and methylmagnesium iodide as a pale yellow oil with b.p. 196-8^{o}C/ 3 mm Hg. ^{1}H NMR spectrum, δ (CD_2Cl_2):

1.87 (m, 9H, C_4H_9), 2.09 (d, 3H, J = 6.4 Hz, CH(OH)C$\underline{H}_3$), 3.08 (s, 1H, OH), 6.08 (q, 1H, J = 6.4 Hz, C$\underline{H}$(OH)CH_3), 7.45 (m, 4H, C_4H_9).

Phenyl(2-butyldichlorotellurophenyl)methanol (2e). Through a solution of alcohol **3b** (7.36 g, 20 mmol) in CCl_4 (50 mL), chlorine was passed at 0°C until the initial yellow color disappeared. The solvent was removed under vacuum, and an oily residue was solidified on treatment with hexane. After recrystallization from benzene - hexane, 1:1, compound **2e** was isolated as colorless needles (Table 1).

Dichlorides **2h,l** (Table 1) were obtained from alcohols **3c,d**, respectively following the procedure analogous to that for **2e**. Compound **2a** was not isolated in a pure state due to its partial dehydrohalogenation on recrysatllization.

2-(Butyldibromotelluro)benzyl alcohol (2b). A solution of bromine (6.14 g, 38.4 mmol) in CCl_4 (5 mL) was cooled to -10°C and added dropwise at -10°C to a solution of alcohol **3a** (11.8 g, 38.4 mmol) in CCl_4 (10 mL) under stirring. The mixture was kept at -10°C for 12 h, and the crystalline precipitate formed was filtered off and dried. Analytically pure sample of **2b** as lemon yellow crystals was obtained on recrystallization from carbon tetrachloride - ether, 1:1 (Table 1).

Dibromides **2f,i,m** (Table 1) were obtained from alcohols **3b-d**, respectively following the procedure analogous to that for **2b**.

2-(Butyldiidotelluro)benzyl alcohol (2c). To a suspension of finely powdered iodine (10.2 g, 40 mmol) in chloroform (50 mL), a solution of alcohol **3a** (11.7 g, 40 mmol) in chloroform (10 mL) was added dropwise under stirring at room temperature. The mixture was heated at 90°C until iodine was dissolved and the violet color of the mixture turned red. The solvent was evaporated, and a red oily residue was solidified by treatment with hexane. Analytically pure sample of **2c** as red crystals was obtained on recrystallization from carbon tetrachloride - ether, 1:2 (Table 1).

Diiodides **2g,k,m** (Table 1) were obtained from alcohols **3b-d**, respectively following the procedure analogous to that for **2c**.

1-Butyl-1-chloro-3*H*-benzo-2,1-oxatellurole (1a). The crude 2-butyldichlorotellurobenzyl alcohol (**2a**), obtained by oxidation of a solution of **3a** (11.7 g, 40 mmol) in CCl_4 (50 mL) with dry chlorine followed by evaporation of the solvent, was dissolved in ether (200 mL), and the solution was passed through a column (3.3 x 15 cm) filled with Al_2O_3. The column was washed with ether (100 mL), and the combined ethereal solutions were dried (Na_2SO_4). The solvent (250 mL) was removed under vacuum, and the precipitate filtered off as colorless crystals (Table 2).

Benzoxatelluroles **1e,h,l** (Table 2) were obtained from dichlorides **2e,h,l**, respectively following the procedure analogous to that for **1a**.

1-Butyl-1-bromo-3*H*-benzo-2,1-oxatellurole (1b). To a solution of alcohol **2b** (2.44 g, 5.4 mmol) in benzene (10 mL), triethylamine (0.56 g, 5.5 mmol) was added under stirring at room temperature. The mixture was self-warmed up spontaneously, and triethylammonium hydrobromide precipitated immediately. The precipitate (0.9 g, 100% yield) was filtered off, and the filtrate was washed with water (2 x 15 mL), dried,

evaporated to the volume of 4 mL, and diluted with ether (6 mL) and hexane (2 mL). The mixture was cooled to 0°C, and the precipitate formed was filtered off and recrystallized from acetonitrile to give colorless needles of **1b** (Table 2).

Bromobenzoxatelluroles **1f,i,m** were obtained from dibromides **2f,i,m**, and iodobenzotelluroles **1c,g,k,n** from diiodides **2c,g,k,n** (Table 2) respectively, following the procedure analogous to that for **1a**.

1-Butyl-1-fluoro-3*H*-benzo-2,1-oxatellurole (1d). A mixture of dibromide **2b** (8.13 g, 18 mmol) in $CHCl_3$ (50 mL) and aqueous solution of silver(I) fluoride, obtained from stoichiometric amounts of silver(I) carbonate and 40% HF and used *in situ*, was shaken at room temperature for 40 min. The yellow precipitate of silver(I) bromide (6.75 g, 100% yield) was filtered off, the organic layer of filtrate separated, dried (Na_2SO_4), and the solvent removed under vacuum. The yellowish oily residue was dissolved in ether (50 mL) and passed through a column filled with Al_2O_3. The eluate was evaporated to give **1d** as a colorless oil (Table 2).

2-(Butyldibromotelluro)benzaldehyde (4a). To a solution of oxatellurole **1b** (3.70 g, 10 mmol) in CCl_4 (40 mL), bromine (1.60 g, 10 mmol) was added in one portion, and the mixture was refluxed until the evolution of HBr stopped and the red color of bromine disappeared (~ 5 h). The solvent was removed, and an oily yellow residue solidified on treatment with hexane. Aldehyde **4a** was obtained in 95% yield as light yellow needles, m.p. 150-152°C (from methanol). ^1H NMR spectrum, δ ($CDCl_3$): 7.89 (m, C_6H_4), 10.09 (s, CHO). Found: C, 29.23; H, 3.03. $C_{11}H_{14}Br_2OTe$ requires: C, 29.38; H, 3.14.

2-Butyldibromotelluro(4′-methyl)benzophenone (4c). Following a procedure analogous to that for **4a**, benzophenone **4c** was obtained from oxatellurole **1i** in 73% yield as orange needles. M.p. 123-125°C (from dioxane - hexane, 1:1). ^1H NMR spectrum, δ ($CDCl_3$): 2.26 (m, C_4H_9), 2.41 (s, CH_3), 8.09 (m, Ph and C_6H_4). Found: C, 39.46; H, 3.69. $C_{18}H_{20}Br_2OTe$ requires: C, 40.05; H, 3.73.

2-Butyldibromotellurobenzophenone **4b** was obtained from oxatellurole **1f** in 79% yield following a procedure analogous to that for **4a**. M.p. 156-158°C (from chloroform - hexane, 1:1). ^1H NMR spectrum, δ ($CDCl_3$): 2.38 (m, C_4H_9), 8.21 (m, Ph and C_6H_4). Found: C, 38.62; H, 3.29. $C_{17}H_{18}Br_2OTe$ requires: C, 38.83; H, 3.45.

2-(Butyldibromotelluro)-ω,ω-dibromoacetophenone (7c). To a refluxing solution of bromine (3.20 g, 20 mmol) in CCl_4 (50 mL), a solution of oxatellurole **1m** (3.86 g, 10 mmol) in CCl_4 (10 mL) was added dropwise under stirring. The mixture was refluxed until the evolution of HBr stopped, the color of bromine disappeared and the yellow precipitate formed (~ 10 min). The solvent was removed, and a dry residue was recrystallized from benzene 5 times. Ketone **7c** was obtained in 35 % yield as large yellow crystals with m.p. 162-165°C. ^1H NMR spectrum, δ ($CDCl_3$): 2.33 (m, C_4H_9), 6.16 (s, CH), 8.15 (m, C_6H_4). Found: C, 23.05; H, 2.11. $C_{12}H_{14}Br_4OTe$ requires: C, 23.19; H, 2.27.

2-(Tribromotelluro)benzaldehyde (8). To a solution of oxatellurole **1b** (15.7 g, 42.3 mmol) in glacial acetic acid (50 mL), bromine (13.54 g, 86.4 mmol) was added at 50°C, and the mixture was refluxed for 10 min. The mixture was cooled to 5°C and diluted with equal volume of ether. Precipitated as small golden plates

aldehyde **8** (12.6 g, 63%) was filtered off and dried. M.p. 228-230°C. Found: C, 17.55; H, 1.01. $C_7H_5Br_3OTe$ requires: C, 17.80; H, 1.07.

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