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

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**Key Words:** *o*-Alkyltellurobenzaldehydes, *o*-Alkyltellurophenylketones; *o*-Alkyltellurobenzyl alcohols;  
3H(3R)-Benzo-2,1-oxatelluroles.

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

### INTRODUCTION

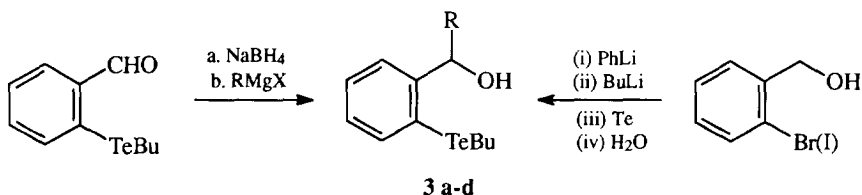
The characteristic reactivity of organotellurium compounds, especially the facile heterolysis of C-Te bond and the tendency of Te(II) derivatives to undergo oxidative addition, results in the simultaneous modification or even expulsion of a tellurium-containing substituents under the conditions of various transformations of organic functionalities<sup>1</sup>. For this reason, attempts to obtain *o*-methyltellurobenzaldehyde<sup>2</sup> or *o*-methyltelluroacetophenone<sup>3</sup> 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<sub>2</sub>. Aromatic aldehydes<sup>2</sup> and ketones<sup>3,4</sup>, containing an *o*-alkyltelluro substituent, have been obtained by insertion of Te into the C-Li bonds of the correspondingly protected *o*-lithiobenzaldehyde<sup>2</sup>, *o*-lithioacetophenone<sup>3</sup> or *o*-lithioacetophenone<sup>4</sup> 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-chlorotellurenyl-benzophenone with dimethylcadmium<sup>5</sup>. *o*-Phenyltellurobenzophenone has also been prepared by the  $S_{RN}1$  reaction of *o*-bromobenzophenone with phenyltelluroate anion generated by electrochemical reduction of diphenyl ditelluride<sup>6</sup>.

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*(3*R*)-benzo-2,1-oxatellurole.

## RESULTS AND DISCUSSION

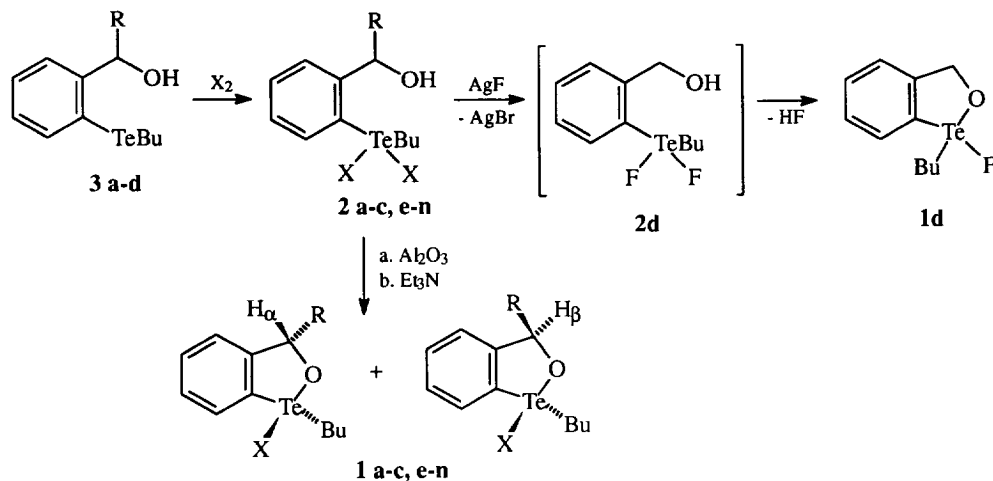
1-Halogeno-1-butyl-3*H*-benzo-2,1-oxatelluroles **1** were obtained in high yields by dehydrohalogenation of 2-butyldihalogenotellurobenzyl alcohols **2a-d** or their derivatives **2e-n** (Table 1). Compounds **2a-n** were prepared by oxidation of the corresponding benzyl alcohols **3a-d** with halogens. The alcohols **3a-d** were synthesized from 2-butylditellurobenzaldehyde in 70-90% yields: **3a** by reduction with NaBH<sub>4</sub>, and **3b-d** by coupling with the Grignard reagents<sup>7,8</sup>. The alternative approach to 2-butylditellurobenzyl 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<sup>8</sup>. The yields of **3a** were 55% and 60% respectively.



**3 a** R = H; **b** R = Ph; **c** R = 4-MeC<sub>6</sub>H<sub>4</sub>; **d** R = Me

The terms of dehydrohalogenation 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-butyldichlorotellurobenzyl alcohol **2a** was passed through a column filled with aluminum oxide, or on treatment with the equimolar amount of

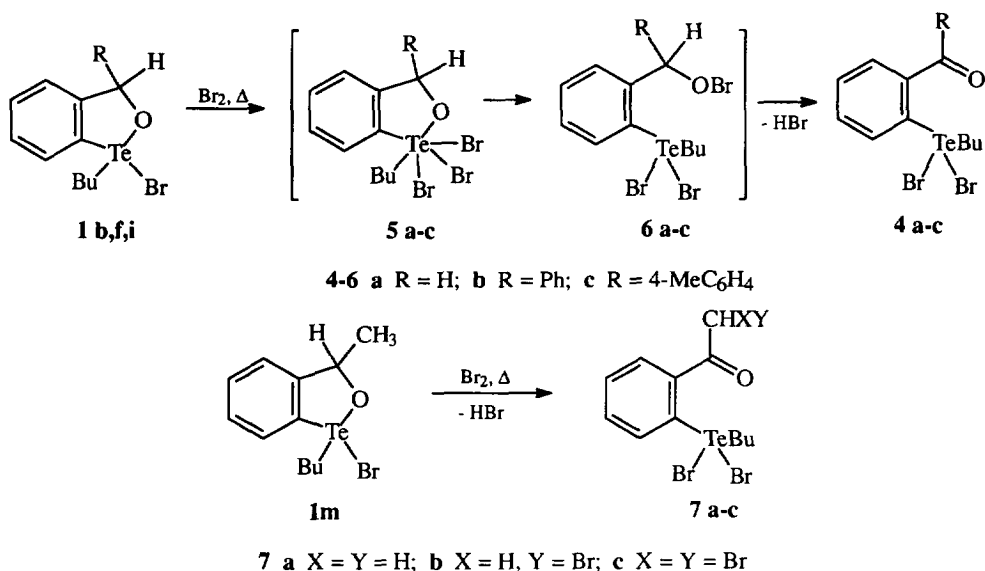
triethylamine. A treatment with triethylamine was also a necessary step in cyclization of dibromo and diiodo derivatives **2b,c**.



**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<sub>6</sub>H<sub>4</sub>, X = Cl; **i** R = 4-MeC<sub>6</sub>H<sub>4</sub>, X = Br; **k** R = 4-MeC<sub>6</sub>H<sub>4</sub>, 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 <sup>1</sup>H 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<sub>2</sub> 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<sup>7,8</sup>. 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.



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

The interaction of one mole of benzotellurolole **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.

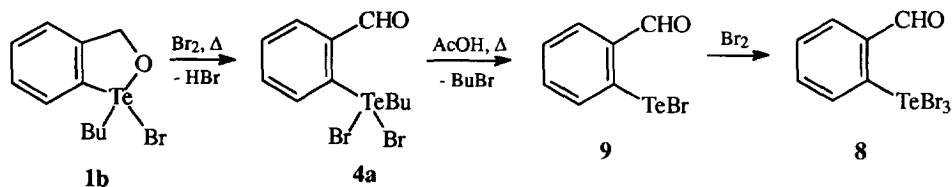


Table 1. Characteristics of Alcohols **2 b-n**.

Compd	Mp (°C)	<sup>1</sup> H NMR, δ, ppm	Molecular formula	Found (requires), % C H	Yield, %
<b>2b</b>	94-96	2.37 (m, C <sub>4</sub> H <sub>9</sub> ), 3.15 (s, OH), 5.04 (s, CH <sub>2</sub> ), 7.55 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>11</sub> H <sub>16</sub> Br <sub>2</sub> OTe	29.10 (29.25) 3.42 (3.57)	83
<b>2c</b>	108-110	2.19 (m, C <sub>4</sub> H <sub>9</sub> ), 2.67 (s, OH), 4.91 (s, CH <sub>2</sub> ), 7.42 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>11</sub> H <sub>16</sub> I <sub>2</sub> OTe	24.31 (24.17) 2.83 (2.95)	60
<b>2e</b>	137-139	2.48 (m, C <sub>4</sub> H <sub>9</sub> ), 3.45 (s, OH), 6.42 (s, CH <sub>2</sub> ), 7.68 (m, Ph and C <sub>6</sub> H <sub>4</sub> )	C <sub>17</sub> H <sub>20</sub> Cl <sub>2</sub> OTe	46.38 (46.53) 4.41 (4.59)	64
<b>2f</b>	143-145	2.40 (m, C <sub>4</sub> H <sub>9</sub> ), 3.39 (s, OH), 6.37 (s, CH <sub>2</sub> ), 7.48 (m, Ph and C <sub>6</sub> H <sub>4</sub> )	C <sub>17</sub> H <sub>20</sub> Br <sub>2</sub> OTe	38.58(38.70) 3.75(3.82)	77
<b>2g</b>	119-122	2.26 (m, C <sub>4</sub> H <sub>9</sub> ), 3.28 (s, OH), 6.21 (s, CH <sub>2</sub> ), 7.38 (m, Ph and C <sub>6</sub> H <sub>4</sub> )	C <sub>17</sub> H <sub>20</sub> I <sub>2</sub> OTe	33.01(32.84) 3.15(3.24)	66
<b>2h</b>	128-129	-	C <sub>18</sub> H <sub>22</sub> Cl <sub>2</sub> OTe	47.68(47.74) 4.66(4.90)	63
<b>2i</b>	135-137	2.10 (m, C <sub>4</sub> H <sub>9</sub> ), 2.32, 2.34 (two s, CH <sub>3</sub> ), 6.29, 6.70 (two s, CH), 7.48 (m, two C <sub>6</sub> H <sub>4</sub> )	C <sub>18</sub> H <sub>22</sub> Br <sub>2</sub> OTe	39.69(39.91) 4.20(4.09)	86
<b>2k</b>	118-119	-	C <sub>18</sub> H <sub>22</sub> I <sub>2</sub> OTe	33.92(34.00) 3.55(3.49)	54
<b>2l</b>	92-94	2.45 (m, C <sub>4</sub> H <sub>9</sub> ), 1.75 (d, CH <sub>3</sub> , <i>J</i> =6.9 Hz), 3.50 (s, OH), 5.46 (q, CH, <i>J</i> =6.9 Hz), 7.68 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>12</sub> H <sub>18</sub> Cl <sub>2</sub> OTe	38.25(38.07) 4.77(4.82)	65
<b>2m</b>	102-105	2.35 (m, C <sub>4</sub> H <sub>9</sub> ), 1.66 (d, CH <sub>3</sub> , <i>J</i> =6.8 Hz), 3.13 (s, OH), 5.38 (q, CH, <i>J</i> =6.8 Hz), 7.63 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>12</sub> H <sub>18</sub> Br <sub>2</sub> OTe	31.04(30.95) 4.25(3.90)	72
<b>2n</b>	112-115	2.18 (m, C <sub>4</sub> H <sub>9</sub> ), 1.50 (d, CH <sub>3</sub> , <i>J</i> =6.8 Hz), 3.05 (s, OH), 5.20 (q, CH, <i>J</i> =6.8 Hz), 7.50 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>12</sub> H <sub>18</sub> I <sub>2</sub> OTe	26.00(25.75) 3.18(3.24)	70

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

Compd	Mp (°C)	<sup>1</sup> H NMR, δ, ppm	Molecular formula	Found (requires), % C H	Yield, %
<b>1a</b>	114-115	1.79 (m, C <sub>4</sub> H <sub>9</sub> ), 5.32 (d, 1H, CH <sub>2</sub> , <i>J</i> = 14.4 Hz), 5.32 (d, 1H, CH <sub>2</sub> , <i>J</i> = 14.4 Hz), 7.68 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>11</sub> H <sub>15</sub> ClOTe	40.29 (40.49) 4.70 (4.63)	89
<b>1b</b>	113-114	1.96 (m, C <sub>4</sub> H <sub>9</sub> ), 5.27 (d, 1H, CH <sub>2</sub> , <i>J</i> = 14.8 Hz), 5.55 (d, 1H, CH <sub>2</sub> , <i>J</i> = 14.8 Hz), 7.80 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>11</sub> H <sub>15</sub> BrOTe	35.45 (35.64) 3.99 (4.08)	78
<b>1c</b>	110-112	2.19 (m, C <sub>4</sub> H <sub>9</sub> ), 5.31 (d, 1H, CH <sub>2</sub> , <i>J</i> = 15.0 Hz), 5.61 (d, 1H, CH <sub>2</sub> , <i>J</i> = 15.0 Hz), 7.72 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>11</sub> H <sub>15</sub> IOTe	31.35 (31.63) 3.51 (3.62)	75
<b>1d</b>	oil	1.83 (m, C <sub>4</sub> H <sub>9</sub> ), 5.46 (dd, <i>J</i> = 15.2 Hz, 3-H), 7.80 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>11</sub> H <sub>15</sub> FOTe	42.35 (42.64) 4.65 (4.88)	85
<b>1e</b>	127-128	2.27 (m, C <sub>4</sub> H <sub>9</sub> ), 6.40, 6.71 (two s, 3-H <sub>α</sub> and 3-H <sub>β</sub> ), 7.91 (m, Ph and C <sub>6</sub> H <sub>4</sub> )	C <sub>17</sub> H <sub>19</sub> BrOTe	51.02(50.74) 4.55(4.76)	70
<b>1f</b>	138-139	2.11 (m, C <sub>4</sub> H <sub>9</sub> ), 6.28, 6.57 (two s, 3-H <sub>α</sub> and 3-H <sub>β</sub> ), 7.75 (m, Ph and C <sub>6</sub> H <sub>4</sub> )	C <sub>17</sub> H <sub>19</sub> BrOTe	45.35(45.69) 4.56(4.29)	82
<b>1g</b>	140-142	1.99 (m, C <sub>4</sub> H <sub>9</sub> ), 6.17, 6.42 (two s, 3-H <sub>α</sub> and 3-H <sub>β</sub> ), 7.00 (m, Ph and C <sub>6</sub> H <sub>4</sub> )	C <sub>17</sub> H <sub>19</sub> IOTe	41.10(41.35) 3.24(3.88)	86
<b>1h</b>	140-141	2.22 (m, C <sub>4</sub> H <sub>9</sub> ), 2.42 (s, CH <sub>3</sub> ), 6.38, 6.78 (two s, 3-H <sub>α</sub> and 3-H <sub>β</sub> ), 7.87 (m, two C <sub>6</sub> H <sub>4</sub> )	C <sub>18</sub> H <sub>21</sub> ClOTe	51.73(51.95) 5.15(5.08)	79
<b>1i</b>	138-140	2.05 (m, C <sub>4</sub> H <sub>9</sub> ), 2.33 (s, CH <sub>3</sub> ), 6.29, 6.70 (two s, 3-H <sub>α</sub> and 3-H <sub>β</sub> ), 7.78 (m, two C <sub>6</sub> H <sub>4</sub> )	C <sub>18</sub> H <sub>21</sub> BrOTe	47.17(46.91) 4.65(4.59)	84
<b>1k</b>	100-102	1.98 (m, C <sub>4</sub> H <sub>9</sub> ), 2.26 (s, CH <sub>3</sub> ), 6.10, 6.65 (two s, 3-H <sub>α</sub> and 3-H <sub>β</sub> ), 7.60 (m, two C <sub>6</sub> H <sub>4</sub> )	C <sub>18</sub> H <sub>21</sub> IOTe	42.50(42.57) 3.89(4.17)	62
<b>1l</b>	124-125	2.12 (m, C <sub>4</sub> H <sub>9</sub> ), 1.52 (d, CH <sub>3</sub> , <i>J</i> = 6.1 Hz), 5.64, 5.92 (two q, 3-H <sub>α</sub> and 3-H <sub>β</sub> , <i>J</i> = 6.1 Hz), 7.97 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>12</sub> H <sub>17</sub> ClOTe	42.48(42.35) 5.21(5.04)	81
<b>1m</b>	116-118	2.01 (m, C <sub>4</sub> H <sub>9</sub> ), 1.47 (d, CH <sub>3</sub> , <i>J</i> = 6.0 Hz), 5.48, 5.75 (two q, 3-H <sub>α</sub> and 3-H <sub>β</sub> , <i>J</i> = 6.0 Hz), 7.84 (m, C <sub>6</sub> H <sub>4</sub> )	C <sub>12</sub> H <sub>17</sub> BrOTe	37.14(37.46) 4.30(4.45)	85
<b>1n</b>	120-121		C <sub>12</sub> H <sub>17</sub> 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*(3*R*)-benzo-2,1-telluroles, was developed. The rearrangement of 3*H*(3*R*)-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. <sup>1</sup>H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) using CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane as internal reference. The solvents used were dried and distilled in accordance with the standard procedures. 2-Butyltellurobenzaldehyde was prepared according to the literature procedure<sup>2</sup>.

### 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°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°C. The mixture was stirred at 8-10°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<sub>2</sub>), and the solvent removed under vacuum. The residue was distilled *in vacuo* (175-8°C/2 mm Hg) to give **3a** as a pale yellow oil in 85% yield. <sup>1</sup>H NMR spectrum, δ (CDCl<sub>3</sub>): 1.87 (m, 9H, C<sub>4</sub>H<sub>9</sub>), 3.02 (s, 1H, OH), 4.64 (s, 2H, CH<sub>2</sub>OH), 7.64 (m, 4H, C<sub>6</sub>H<sub>4</sub>). Found: C, 45.04; H, 5.41. C<sub>11</sub>H<sub>16</sub>O<sub>Te</sub> 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 (5 mL), a solution of NaBH<sub>4</sub> (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<sub>2</sub>SO<sub>4</sub>). 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-methylphenylmagnesium bromides, respectively and used without isolation for further oxidation into alcohols **2e-1**.

1-(2-Butyltellurophenyl)ethanol (**3d**) was synthesized from 2-butyltellurobenzaldehyde and methylmagnesium iodide as a pale yellow oil with b.p. 196-8°C/ 3 mm Hg. <sup>1</sup>H NMR spectrum, δ (CD<sub>2</sub>Cl<sub>2</sub>):

1.87 (m, 9H, C<sub>4</sub>H<sub>9</sub>), 2.09 (d, 3H,  $J = 6.4$  Hz, CH(OH)CH<sub>3</sub>), 3.08 (s, 1H, OH), 6.08 (q, 1H,  $J = 6.4$  Hz, CH(OH)CH<sub>3</sub>), 7.45 (m, 4H, C<sub>4</sub>H<sub>9</sub>).

**Phenyl(2-butyldichlorotellurophenyl)methanol (2e).** Through a solution of alcohol **3b** (7.36 g, 20 mmol) in CCl<sub>4</sub> (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 recrystallization.

**2-(Butyldibromotelluro)benzyl alcohol (2b).** A solution of bromine (6.14 g, 38.4 mmol) in CCl<sub>4</sub> (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<sub>4</sub> (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-(Butyldiiodotelluro)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-3H-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<sub>4</sub> (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<sub>2</sub>O<sub>3</sub>. The column was washed with ether (100 mL), and the combined ethereal solutions were dried (Na<sub>2</sub>SO<sub>4</sub>). 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-3H-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<sub>3</sub> (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<sub>2</sub>SO<sub>4</sub>), and the solvent removed under vacuum. The yellowish oily residue was dissolved in ether (50 mL) and passed through a column filled with Al<sub>2</sub>O<sub>3</sub>. 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<sub>4</sub> (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). <sup>1</sup>H NMR spectrum, δ (CDCl<sub>3</sub>): 7.89 (m, C<sub>6</sub>H<sub>4</sub>), 10.09 (s, CHO). Found: C, 29.23; H, 3.03. C<sub>11</sub>H<sub>14</sub>Br<sub>2</sub>OTe 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). <sup>1</sup>H NMR spectrum, δ (CDCl<sub>3</sub>): 2.26 (m, C<sub>4</sub>H<sub>9</sub>), 2.41 (s, CH<sub>3</sub>), 8.09 (m, Ph and C<sub>6</sub>H<sub>4</sub>). Found: C, 39.46; H, 3.69. C<sub>18</sub>H<sub>20</sub>Br<sub>2</sub>OTe 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). <sup>1</sup>H NMR spectrum, δ (CDCl<sub>3</sub>): 2.38 (m, C<sub>4</sub>H<sub>9</sub>), 8.21 (m, Ph and C<sub>6</sub>H<sub>4</sub>). Found: C, 38.62; H, 3.29. C<sub>17</sub>H<sub>18</sub>Br<sub>2</sub>OTe 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<sub>4</sub> (50 mL), a solution of oxatellurole **1m** (3.86 g, 10 mmol) in CCl<sub>4</sub> (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. <sup>1</sup>H NMR spectrum, δ (CDCl<sub>3</sub>): 2.33 (m, C<sub>4</sub>H<sub>9</sub>), 6.16 (s, CH), 8.15 (m, C<sub>6</sub>H<sub>4</sub>). Found: C, 23.05; H, 2.11. C<sub>12</sub>H<sub>14</sub>Br<sub>4</sub>OTe 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<sub>7</sub>H<sub>5</sub>Br<sub>3</sub>OTe requires: C, 17.80; H, 1.07.

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