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5H-1,2-OXATELLUROLES AND THEIR BENZO ANALOGS: SYNTHESIS AND REACTIONS

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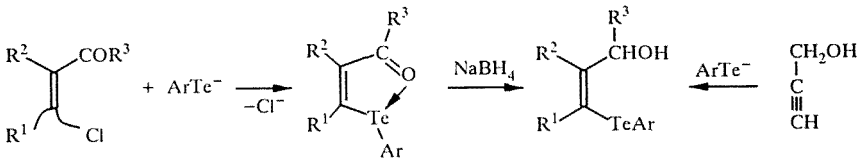
Tetracoordinated derivatives of 2-halo-2-aryl-5H-1,2-oxatelluroles and 1-halo-1-butyl-3H-benz-2,1-oxatelluroles were synthesized by the oxidation of 3-aryltelluro-2-propen-1-ols and the dehydrogenation of 2-butyldihalotellurobenzyl alcohols. The halogen atoms in these compounds are readily replaced in nucleophilic substitution reactions. The reaction of benzoxatelluroles with bromine is accompanied by cleavage of O—Te bonds and leads, depending on the nature of the substituent at $C_{(3)}$, to 2-(butylbromotelluro)benzaldehyde or 2-(butyldibromotelluro)benzophenone.

Five-membered tellurium 1,2-heterocycles [1, 2] have been subjected to much less investigation than their sulfur and selenium analogs. Only mesionic tellurium—oxygen halides of this type obtained by Detty and Murray [3, 4] by the thermal or $AlCl_3$—catalyzed rearrangement of β-aryltelluropropenoyl chlorides have been studied in considerable detail.

In the present work, we studied methods for the synthesis and several reactions of tetracoordinated derivatives of new heterocyclic systems, namely, 5H-1,2-oxatellurole (I) and 3H-benz-2,1-oxatellurole (II). Preliminary communications on the synthesis of these compounds have already appeared [5, 6].

3-(Aryltelluro)-2-propen-1-ols (III) and 2(butyltelluro)benzyl alcohols (IV) were used as the precursors for these heterocycles. Propenols (III) were synthesized either by nucleophilic addition of aryltellurolate anions at the triple bond of propargyl alcohol (this reaction has been studied previously only with the phenyltellurolate anion [7, 8]) and reduction of β-aryltelluro-α,β-unsaturated aldehydes and ketones (V). The synthesis of products (V) may be achieved by the nucleophilic addition of aryltellurolate anions to α-acetylenic aldehydes or ketones in accord with the work of Buzilova, et al. [9, 10]. However, this method has some disadvantages since the substituent at the α-carbon atom must be hydrogen. Thus, the previously unreported nucleophilic exchange of the chlorine atoms in readily available β-chlorovinyl aldehydes and ketones (VI) by aryltellurolate anions was used for the synthesis of V. These reactions were carried out by treating VI in THF with aryltellurolate anions at reduced temperature. Tellurolate anions were generated either by the reaction of phenyllithium with powdered tellurium or the reduction of di(4-ethoxyphenyl) ditelluride by lithium in the presence of catalytic amounts of naphthalene. Both methods for obtaining lithium tellurophenolates give comparable results and permit us to synthesize V in 37-57% yield.



VI a-c V a-e III a-g

III a-c, V a-c Ar = C_6H_5; a $R^1 = C_6H_5$, $R^2 = R^3 = H$; b $R^1 + R^2 = (CH_2)_4$, $R^3 = H$; c $R^1 = R^2 = H$, $R^3 = C_6H_5$; IIId,e Vd,e Ar = 4-$C_2H_5OC_6H_4$, d $R^1 = C_6H_5$, $R^2 = R^3 = H$; d $R^1 + R^2 = (CH_2)_4$, $R^3 = H$; IIIf-h $R^1 = R^2 = R^3 = H$; f Ar = C_6H_5; g Ar = 4-$CH_3OC_6H_4$; i Ar = 4-$C_2H_5OC_6H_4$; VIa,b $R^3 = H$; a $R^1 = C_6H_5$, $R^2 = H$; b $R^1 + R^2 = (CH_2)_4$; c $R^1 = R^2 = H$, $R^3 = C_6H_5$

Physical and Organic Chemistry Research Institute, Rostov State University, Rostov-on-the-Don 344104. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 266-279, February, 1994. Original article submitted December 22, 1993.

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TABLE 1. Physical Indices of Oxatelluroles Ia-Ii

Compound	Empirical formula	mp, °C	PMR spectra, ppm (J), Hz	Yield, %
Ia	$C_{15}H_{13}ClOTe$	115	—	79
Ib	$C_{13}H_{15}ClOTe$	118,5	2,13 (8H, m, $4CH_2$), 4,90 (2H, dd., J = 17,0, 3-H), 7,63 (5H, m, C_6H_5)	82
Ic	$C_{15}H_{13}ClOTe$	126	6,02 and 6,26 (1H, s, s, 3α or β-H), 7,45 (12H, m, $2C_6H_5$ + CH = CH)	78
Id	C_9H_9ClOTe	128	5,27 (2H, dd, J = 17,8, CH_2), 7,54 (7H, m, C_6H_5 + CH = CH)	44
Ie	$C_{17}H_{17}ClO_2Te$	130,5	1,40 (3H, t, CH_3), 4,05 (2H, q, OCH_2), 5,18 (2H, dd, J = 18,0, 3-H), 7,44 (10H, m, C_6H_5 + C_6H_4 + 4-H)	75
If	$C_{11}H_{13}ClO_2Te$	115	1,40 (3H, t, CH_3), 4,04 (2H, q, OCH_2), 5,18 (2H, dd, J = 18,1, 3-H), 6,96 (2H, d, 3′-,5′-H), 7,32 (2H, m, CH = CH), 8,12 (2H, d 2′-, 6′-H)	45
Ig	$C_{10}H_{11}ClO_2Te$	118	3,81 (3H, s, OCH_3), 5,17 (2H, dd, J = 18,1, 3-H), 6,97 (2H, d, 3′-,5′-H), 7,30 (2H, m, CH = CH), 7,82 (2H, d, 2′-,6′-H)	47
Ih	C_9H_9IOTe	120	5,15 (2H, dd, J = 18,0, CH_2), 7,59 (7H, m, C_6H_5 + CH = CH)	82
Ii	$C_{11}H_{13}IO_2Te$	104	1,40 (3H, t, CH_3), 4,03 (2H, q, OCH_2), 5,25 (2H, dd, J = 18,5, 3-H), 7,37 (6H, m, C_6H_4 + CH = CH)	84

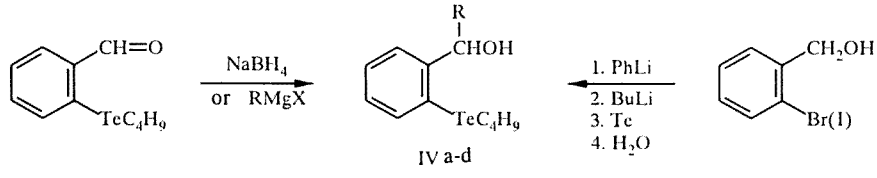
The compositions and structures of V were indicated by elemental analysis, PMR spectroscopy, and several chemical transformations such as reduction to give alcohols III.

In addition to cyclohexene derivatives Vb and Ve, which naturally have *cis* configuration, an unequivocal conclusion concerning structure may also be made for 1-phenyl-3-(phenyltelluro)propen-1-one (Vc). The coupling constant of the olefinic protons in the PMR spectrum of this compound is 8.79 Hz, which is in the range for *cis* olefins (6-12 Hz) [11]. Since the sp^2-hybridized oxygen and nitrogen atoms in the *ortho* positions of the aromatic rings and at the 2-positions of the olefinic systems form strong O(N)→Te chelation bonds with the tellurium atoms, which stabilize organotellurium compounds [3, 12, 13], we may assume that the conformation shown in the scheme is favored in solution and the crystalline state for all V. This conclusion should be checked by dipole moment measurements and x-ray diffraction structural analysis.

Similar to other aldehydes and ketones, V are readily reduced by sodium borohydride to give alcohols IIIa-IIIe.

Alcohols IIIf-IIIh were obtained in yields exceeding 45% by the nucleophilic addition of aryltellurolate anions to propargyl alcohol and the generation of tellurolate anions was carried out by the reduction of the corresponding diaryl tellurides using sodium borohydride in ethanol or 2-propanol [5]. This reaction proceeds regiospecifically and stereospecifically, as in the addition of tellurolate anions to acetylenes RC≡CH [7, 8, 14, 15], including the addition of phenyltellurolate anion to propargyl alcohol [7, 8, 14], and gives *Z* isomers of III.

The preparation of 2-butyltellurobenzyl alcohols IV was carried out by the reduction of 2-butyltellurobenzaldehyde with sodium borohydride or its reaction with Grignard reagents in 70-90% yields. An alternative method for the synthesis of 2-butyltellurobenzyl alcohol (IVa) involves the reaction of 2-bromo- or 2-iodobenzyl alcohol with two equivalents of butyl lithium and subsequent treatment of the reaction mixture with powdered tellurium and hydrolysis to give alcohol IVa in 55-59% yield [6]. However, a modification of this reaction, in which the organolithium compounds were not previously obtained but rather generated directly in the reaction flask proved more convenient for preparative purposes. The essence of this method lies in the circumstance that a suspension of the required amount of lithium in ether is treated initially with bromobenzene (the resultant phenyllithium converts bromobenzyl alcohol added to the reaction mixture into its lithium derivative), then with butyl bromide, which upon reaction with lithium is converted to butyllithium, which accomplishes the lithiation of lithium 2-bromobenzylate, and finally, with tellurium. In this case not only is the procedure for obtaining alcohol IVa simplified but the yield of this product is raised to 82-85%.



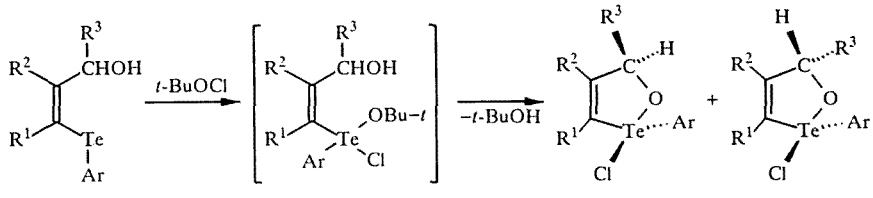
IV a-d

IV a R = H, b R = C_6H_5, c R = 4-$CH_3C_6H_4$, d R = CH_3

TABLE 2. Physical Indices of 2-(Butyldihalotelluro)benzyl Alcohols VIIIb-VIIIm

Compound	Empirical formula	Mp, °C	PMR spectra, ppm (J), Hz	Yield, %
VIIIb	$C_{11}H_{16}Br_2OTe$	94...96	2,37 (9H, m, C_4H_9), 3,15 (1H, s, OH), 5,04 (2H, s, CH_2), 7,55 (4H, m, C_6H_4)	83
VIIIc	$C_{11}H_{16}I_2OTe$	108...110	2,19 (9H, m, C_4H_9), 2,67 (1H, s, OH), 4,91 (2H, s, CH_2), 7,42 (4H, m, C_6H_4)	60
VIIIe	$C_{17}H_{20}Cl_2OTe$	137...139	2,48 (9H, m, C_4H_9), 3,45 (1H, s, OH), 6,42 (1H, s, CH), 7,68 (9H, m, $C_6H_5 + C_6H_4$)	64
VIIIf	$C_{17}H_{20}Br_2OTe$	143...145	2,40 (9H, m, C_4H_9), 3,39 (1H, s, OH), 6,37 (1H, s, CH), 7,48 (9H, m, $C_6H_5 + C_6H_4$)	77
VIIIg	$C_{17}H_{20}I_2OTe$	119...122	2,26 (9H, m, C_4H_9), 3,28 (1H, s, OH), 6,21 (1H, s, CH), 7,38 (9H, m, $C_6H_5 + C_6H_4$)	66
VIIIh	$C_{18}H_{22}Cl_2OTe$	128...129	—	63
VIIIi	$C_{18}H_{22}Br_2OTe$	135...137	—	86
VIIIj	$C_{18}H_{22}I_2OTe$	118...119	—	54
VIIIk	$C_{12}H_{18}Cl_2OTe$	92...94	2,45 (9H, m, C_4H_9), 1,75 (3H, d, CH_3), 3,50 (1H, s, OH), 5,46 (1H, q, CH), 7,68 (4H, m, C_6H_4)	65
VIIIℓ	$C_{12}H_{18}Br_2OTe$	102...105	2,35 (9H, m, C_4H_9), 1,66 (3H, d, CH_3), 3,13 (1H, s, OH), 5,38 (1H, q, CH), 7,63 (4H, m, C_6H_4)	72
VIIIm	$C_{12}H_{18}I_2OTe$	112...115	2,18 (9H, m, C_4H_9), 1,50 (3H, d, CH_3), 3,05 (1H, s, OH), 5,20 (1H, q, CH), 7,50 (4H, m, C_6H_4)	70

The conversion of alcohols III and IV into heterocycles I and II was carried out by two different methods. The first method used mainly for the synthesis of 5H-1,2-oxatelluroles I [5] involves the oxidation of alcohols III by *tert*-butyl hypochlorite. This reaction probably takes place through the intermediate formation of σ-tellurans (VII), which are converted into heterocycles I in 44-82% yield by eliminating a *tert*-butyl alcohol molecule (Table 1).



III a-d, e-h VII Ia-g

Ia—d Ar = C_6H_5, a $R^1 = C_6H_5$, $R^2 = R^3 = H$; b $R^1 + R^2 = (CH_2)_4$, $R^3 = H$; c $R^1 = R^2 = H$, $R^3 = C_6H_5$; d $R^1 = R^2 = R^3 = H$; c,f Ar = 4-$C_2H_5OC_6H_4$, e $R^1 = C_6H_5$, $R^2 = R^3 = H$; f $R^1 = R^2 = R^3 = H$; g Ar = 4-$CH_3OC_6H_4$, $R^1 = R^2 = R^3 = H$

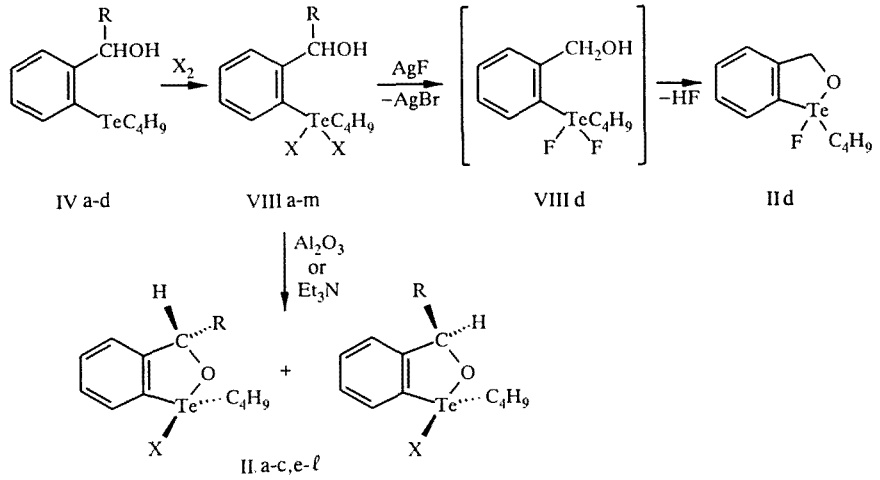
We should note that analytically pure alcohols III were not introduced into the reaction but rather solutions of these compounds in chloroform obtained after treatment of the reaction mixtures upon their synthesis.

Oxatelluroles I are colorless, odorless, crystalline compounds with rather good solubility in polar organic solvents.

The synthesis of benzoxatelluroles II was carried out by dehydrohalogenation of 2-butyldihalotellurobenzyl alcohols (VIII) [6] (Table 2), which were obtained in high yield by the oxidation of alcohols IV with halogens (Cl_2, Br_2, and I_2). In the case of alcohols VIII with R = H, we found that the conditions for the dehalogenation are a function of the nature of the halogens at the tellurium atom. Indeed, 2-butyldifluorotellurobenzyl alcohol (VIIId) obtained by treating 2-butyldibromotellurobenzyl alcohol (VIIIb) with silver fluoride in acetone simultaneously cyclizes to give 1-butyl-1-fluoro-3H-benz-2,1-oxatellurole (IId) in 87% yield. 2-Butyldichlorotellurobenzyl alcohol (VIIIa) was converted to 1-butyl-1-chloro-3H-benz-2,1-oxatellurole (IIa) either by passing its chloroform solution through an alumina column or by treatment with an equimolar amount of triethylamine. On the other hand, the cyclization of dibromides VIIIb, VIIIf, VIIIi, and VIIIℓ and diiodides VIIIc, VIIIg, VIIIj, and VIIIm was accomplished only the action of triethylamine. The use of other bases for the cyclization led to lower yields. We should note that it is more convenient to carry out the final two steps in one flask, i.e., not to separate out the resultant σ-telluroles VIII after oxidation of alcohols IV by halogen but rather treat their solutions with the required

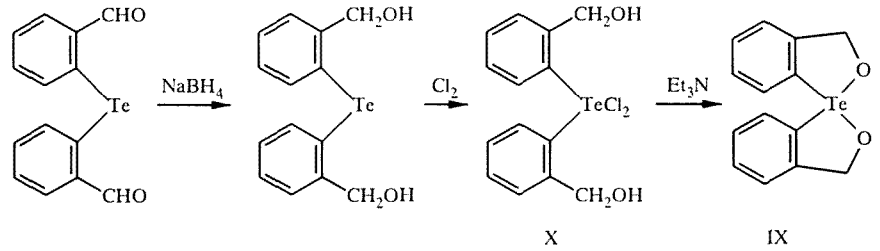
amount of triethylamine. The use of such a procedure has virtually no effect on the yields of heterocycles II (Table 3). Oxa- and benzoxatelluroles containing substituents at $C_{(3)}$ of the heterocycle were obtained as mixtures of two isomers as indicated by their PMR spectra. Thus, the signals for the methine protons in 2-chloro-2,5-diphenyl-1,2-oxatellurole (6.02 and 6.26 ppm) and 2-butyl-2-bromo-5-phenylbenz-2,1-oxatellurole (6.28 and 6.57 ppm) appear as two singlets. On the other hand, the PMR spectrum of 2-butyl-2-bromo-5-methylbenz-1,2-oxatellurole contains two quartets corresponding to the methine proton at 5.48 and 5.75 ppm with 1:1 integral intensity. The content of one of the isomer increases with increasing molecular mass of the halogen. Thus, the isomer ratio for 3-(4-methylphenyl)benzoxatelluroles is 1:2, 1:2.5, and 1:3 in the series Cl, Br, I, respectively.

2,1-Benzoxatelluroles are crystalline solids with the exception of fluorine derivative IId, which is a colorless oil. These derivatives have poor solubility in nonpolar organic solvents but dissolve rather readily in polar organic solvents. All these compounds, independent of the nature of the halogen and substituents at $C_{(3)}$, are colorless although the iodides turn yellow upon storage in the light.



II, VIII a-c R = H; a X = Cl; b X = Br; c X = I; e-g R = C_6H_5; e X = Cl; f X = Br; g X = I; h-j R = 4-$CH_3C_6H_4$, h X = Cl; i X = Br; j X = I; k-m R = CH_3; k X = Cl; ℓ X = Br; m X = I

The procedure developed for the preparation of benzoxatelluroles was used in our previous work for the synthesis of 1,1′-spiro[3H-2,1-benzoxatellurole] (IX) [16]. Treatment of bis(2-hydroxymethylphenyl)tellurium dichloride (X), whose preparation from bis(2-formylphenyl) telluride is shown below, with two equivalents of triethylamine in benzene led to spiran IX in almost quantitative yield.



Michalak, et al. [17] have proposed another approach for the synthesis of 3-substituted spirans IX (3,3,3′,3′-tetramethyl- and 3,3,3′,3′-tetra(trifluoromethyl)-1,1′-spiro[3H-2,1-benzoxatellurole]) based on the reaction of O-magnesium halide derivatives of the corresponding 2-(2-halomagnesium phenyl)propanols with 0.5 equivalent $TeCl_4$. However, the spiran yields are much lower using this method (20-61%).

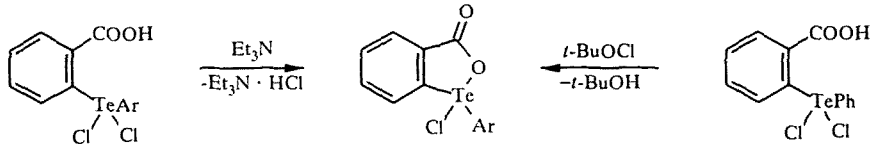
The methylene protons in the PMR spectra of spiran IX appear at room temperature, in contrast to the corresponding protons in the analogous sulfuran [18], as a singlet at 5.28 ppm in deutorochloroform and 5.34 ppm in nitrobenzene. These data, in accord with the results of quantum mechanical calculations [19], indicate a lower activation barrier for polytopic rearrangement of bisphenoidal tellurans in comparison with the analogous sulfur and selenium derivatives.

The methods proposed for the synthesis of oxa- and benzoxatelluroles were also used for the preparation of functional derivatives of the latter. Thus, 1-aryl-1-chlorobenz-2,1-oxatellurol-3-ones (XI) were synthesized in 75-92% yields by the

TABLE 3. Physical Indices of Benzoxatelluroles IIa-IIo

Compound	Empirical formula	Mp, °C	PMR spectra, ppm (J), Hz	Yield, %
IIa	$C_{11}H_{15}ClOTe$	114...115	1,79 (9H, m, C_4H_9), 5,32 (2H, dd, J = 15,3, 3-H), 7,68 (4H, m, C_6H_4)	89
IIb	$C_{11}H_{15}BrOTe$	113...114	1,96 (9H, m, C_4H_9), 5,41 (2H, dd, J = 15,1, 3-H), 7,80 (4H, m, C_6H_4)	78
IIc	$C_{11}H_{15}IOTe$	110...112	2,19 (9H, m, C_4H_9), 5,37 (2H, dd, J = 15,1, 3-H), 7,72 (4H, m, C_6H_4)	75
IId	$C_{11}H_{15}FOTe$	Масло	1,83 (9H, m, C_4H_9), 5,46 (2H, dd, J = 15,2, 3-H), 7,80 (4H, m, C_6H_4)	87
IIe	$C_{17}H_{19}ClOTe$	127...128	2,27 (9H, m, C_4H_9), 6,40 and 6,71 (1H, s, s, 3α or β-H), 7,91 (9H, m, C_6H_5 + C_6H_4)	70
IIf	$C_{17}H_{19}BrOTe$	138...139	2,11 (9H, m, C_4H_9), 6,28 and 6,57 (1H, s, s, 3α or β-H), 7,75 (9H, m, C_6H_5 + C_6H_4)	82
IIg	$C_{17}H_{19}IOTe$	140...142	1,99 (9H, m, C_4H_9), 6,17 and 6,42 (1H, s, s, 3α or β-H), 7,00 (9H, m, C_6H_5 + C_6H_4)	76
IIh	$C_{18}H_{21}ClOTe$	140...141	2,22 (9H, m, C_4H_9), 2,42 (3H, s, 4-CH_3), 6,38 and 6,78 (1H, s,s, 3α or β-H), 7,87 (8H, m, $2C_6H_4$)	79
IIi	$C_{18}H_{21}BrOTe$	138...140	2,05 (9H, m, C_4H_9), 2,33 (3H, s, 4-CH_3), 6,29 and 6,70 (1H, s,s, 3α or β-H), 7,78 (8H, m, $2C_6H_4$)	84
IIj	$C_{18}H_{21}IOTe$	100...102	1,98 (9H, m, C_4H_9), 2,26 (3H, s, 4-CH_3), 6,10 and 6,65 (1H, s,s, 3α or β-H), 7,60 (8H, m, $2C_6H_4$)	62
IIk	$C_{12}H_{17}ClOTe$	124...125	2,12 (9H, m, C_4H_9), 1,52 (3H, d, CH_3), 5,64 and 5,92 (1H, s,s, 3α or β-H), 7,97 (4H, m, C_6H_4)	81
IIℓ	$C_{12}H_{17}BrOTe$	116...118	2,01 (9H, m, C_4H_9), 1,47 (3H, d, CH_3), 5,48 and 5,75 (1H, s,s 3α or β-H), 7,84 (4H, m, C_6H_4)	85
IIm	$C_{12}H_{17}IOTe$	120...121	—	62
IIn	$C_{13}H_8O_3Te$	68...71	1,78 (9H, m, C_4H_9), 2,01 (3H, s, CH_3), 5,40 (2H, dd, J = 15,1, 3-H), 7,53 (4H, m, C_6H_4)	50...95
IIo	$C_{22}H_{30}O_3Te_2$	89...91	1,92 (9H, m C_4H_9), 5,40 (2H, dd, J = 15,2, 3-H), 7,65 (4H, m C_6H_4)	32

oxidation of 2-carboxydiphenyl telluride using *tert*-butyl hypochlorite and dehydrochlorination of 2-(phenyldichlorotelluro)benzoic acid.



XIa–c

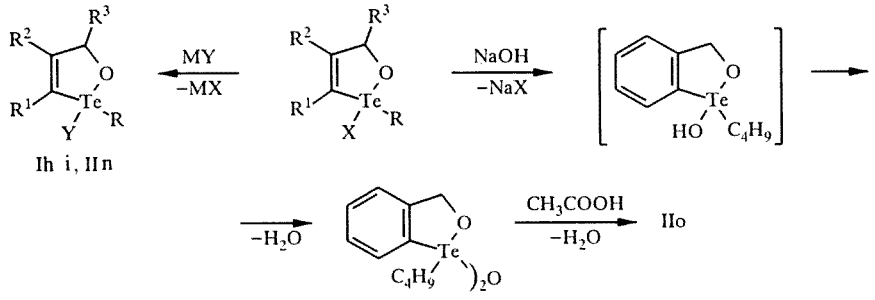
XI a Ar = C_6H_5, b Ar = 4-$CH_3OC_6H_4$, c Ar = 4-$C_2H_5OC_6H_4$

The formation of XI was indicated by disappearance of the broad ν_{OH} band at 3280-3290 cm^{-1} found for the starting acid and shift of the $\nu_{C=O}$ band from 1605-1610 to 1660-1670 cm^{-1}.

A characteristic feature of heterocycles II is their high thermal stability. In contrast to formally analogous arylalkyltellurium dihalides Ar(Alk)$TeHal_2$, which lose alkyl halide quite readily upon heating [20] or upon the action of pyridine [21], heterocycles II do not eliminate a C_4H_9X molecule under the conditions indicated above.

As expected, the halogen atoms in oxa- and benzoxatelluroles are very labile and readily replaced by other anions. Thus, 2-aryl-2-iodo-1,2-oxatelluroles (Ih) and (Ii) were obtained in high yield upon treatment of 2-aryl-2-chloro-1,2-oxatelluroles (If) and (Ig) by potassium iodide in acetone, while the reaction of heterocycle IIb with silver acetate gave 1-butyl-1-acetoxybenz-oxatellurole (In). The reaction of IIb with ethanolic NaOH (or sodium methylate with subsequent treatment of the reaction mixture with water) led to the product of the dehydration of 1-butyl-1-hydroxybenz-2,1-oxatellurole, namely, bis(1-butylbenz-2,1-oxatellurol-1-yl) oxide (IIo), instead of the expected 1-butyl-1-hydroxybenz-2,1-oxatellurole itself. The relatively

low yield of this compound (32%) may be attributed to the cleavage of the heterocyclic fragment along with the exchange reaction. The existence of a Te—O—Te bridge in heterocycle IIo was indicated by the formation of 1-acetoxy derivative IIn upon treatment of the oxide with acetic acid.

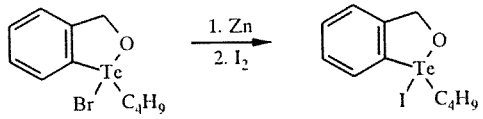


Ih i, IIn

IIn

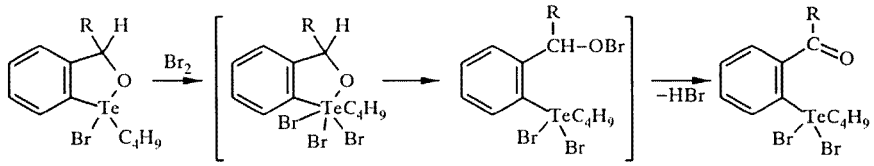
Ih,i $R^1 = R^2 = R^3 = H$, X = I; h R = C_6H_5; i R = 4-$C_2H_5OC_6H_4$; IIn $R^1 + R^2$ = $(CH{=}CH)_2$, R^3 = H, X = $OCOCH_3$, R = C_4H_9

The conversion of some halides II to others was also achieved by reduction of the former with zinc and subsequent treatment of the reaction mixture with 0.5 mole equivalent of the corresponding halogen. Thus, 1-butyl-1-bromobenz-2,1-oxatellurole dissolved almost instantly upon the action of zinc on a solution of this compound in methanol, while the initially colorless solution turned greenish yellow. The replacement of methanol by chloroform and treatment of the solution obtained with a solution of iodine in chloroform led to iodide IIc in virtually quantitative yield. This reaction may proceed either through an organozinc intermediate, TeZnBr, or through tellurium-centered radicals. The formation of free radicals was not observed when this reaction was carried out in the probe of an ESR spectrometer.



IIb IIc

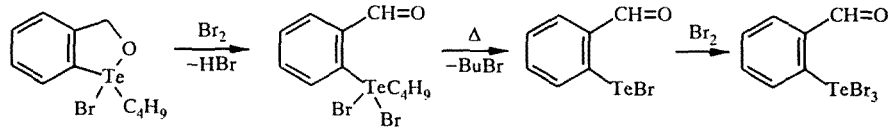
Special interest is found in the reaction of 1-butyl-bromobenz-2,1-oxatelluroles (IIb), (IIf), and (II*l*) with bromine, which proceeds with cleavage of the O—Te bond and leads either to aldehydes [6] or ketones with a $-Te(C_4H_9)Br_2$ group in the *ortho* position, depending on the substituent at $C_{(3)}$. 2-Butyldibromotellurobenzaldehyde (XIIa) is formed in 95% yield in the reaction of heterocycle IIb with an equivalent amount of bromine in chloroform or CCl_4 at reflux. Under analogous conditions, heterocycle IIf is converted to 2-(butyldibromotelluro)benzophenone (XIIb) in 79% yield. As in the case of σ-tellurans [21], XII is reduced by sodium metabisulfite virtually quantitatively to give 2-butyltellurobenzaldehyde and 2-butyltellurobenzophenone. The reactions of benzoxatelluroles with bromine probably proceeds through the intermediate formation of hexacoordinated tellurium derivatives (XIII), whose rearrangement to give intermediates (XIV) with subsequent elimination of HBr leads to carbonyl derivatives XII.



IIb,f XIIIa, b XIVa, b XIIa, b

XII—XIV a R = H, b R = C_6H_5

The use of acetic acid as the solvent and two equivalents of bromine in the latter reaction gives to 2-(tribromotelluro)-benzaldehyde (XV) in yields above 60% yield. We may assume that benzaldehyde IIa formed upon the action of bromine loses a BuBr molecule upon heating in acetic acid to give 2-(bromotellurenyl)benzaldehyde (XVI), whose oxidation by bromine leads to tribromo derivative XV.

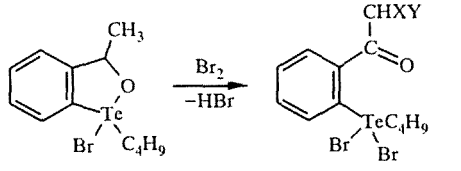


IIb XIIa XVI XV

Evidence for this mechanism is the formation of 2-(bromotellurenyl)benzaldehyde XVI in high yield upon heating an acetic acid solution of 2-(butyldibromotelluro)benzaldehyde in the presence of catalytic amounts of HBr.

Since 3-substituted benzoxatelluroles II are obtained from 2-(butyltelluro)benzaldehyde, while unsubstituted benzoxatellurole is obtained from 2-(butyltelluro)benzyl alcohol, the reaction of benzoxatelluroles with bromine examined above taking account of the reactions used for their preparation may be seen as a new preparative method for the conversion of *o*-(alkyltelluro)benzaldehydes into *o*-(alkyltelluro)benzophenones and of *o*-(alkyltelluro)benzyl alcohols into *o*-(alkyltelluro)-benzaldehydes, which is specific for organotellurium compounds. We should note that attempts to effect the direct oxidation of the Te-methyl analog of alcohol IVd were unsuccessful since they proceeded with cleavage of the C—Te bonds and formation of TeO_2 [22].

The use of the reaction of 3-methyl-2,1-benzoxatellurole (II*l*) with bromine to obtain 2-(bromotellurenyl)acetophenone, which is a precursor to telluroindoxyl [23], holds promise. However, the reaction of heterocycle II*l* with bromine is accompanied by side-reactions, namely, bromination of the methyl group of the initial product, 2-(butyldibromo-telluro)acetophenone (XIIc) to give significant amounts of 2-butyldibromotelluro-ω-bromoacetophenone (XIId). The ratio between dibromide XIIc and tribromide XIId depends on the nature of the solvent. Thus, the ratio is 5:8 when the reaction is carried out in CCl_4 but 1:3 when the reaction is carried out in benzene as indicated by the PMR spectra of the reaction mixtures. When the amount of bromine is increased to two moles per mole heterocycle II*l*, a 1:4.5 mixture of ω-bromoacetophenone XIId and ω,ω-dibromoacetophenone XIIe is formed. Fractional crystallization from benzene gave XIIe as a pure compound.



II*l* XII c-e

XII c-e c X = Y = H; d X = H, Y = Br; e X = Y = Br

EXPERIMENTAL

The PMR spectra were taken on a Varian Unity 300 spectrometer. The IR spectra were taken on a Specord IR-75 spectrometer. Samples of 3-phenyl-3-chloro-1-propenal, 2-chloro-1-cyclohexenecarbaldehyde, and 1-phenyl-3-chloro-2-propen-1-one were obtained as described by Arnold and Zemblicka [26], while diphenyl ditelluride, di(4-methoxyphenyl) ditelluride, and di(4-ethoxyphenyl) ditelluride were obtained according to reported procedures [21, 25, 26]. 2-(Butyltelluro)benzaldehyde and bis(2-formylphenyl) telluride were obtained according to literature methods [16, 27], while 2-carboxyphenyl(aryl)tellurium dichlorides were obtained according to our previous procedure [28].

Elemental analysis data for C, H, and Te for all synthesized compounds corresponded with that calculated.

3-Phenyl-3-(phenyltelluro)-1-propenal (Va, $C_{15}H_{12}OTe$). A solution of phenyllithium obtained from 6.28 g (40 mmoles) bromobenzene and 0.56 g (80 mmoles) lithium in 30 ml ether was added with stirring to a suspension of 5 g (39 mmoles) tellurium powder in 30 ml absolute THF at −10°C in a nitrogen atmosphere. After stirring for 1 h, the temperature was reduced to −15°C and a solution of 5.50 g (33 mmoles) aldehyde VIa in 5 ml THF was added. The mixture was maintained at this temperature for 30 min. The mixture was gradually brought to reflux, heated at reflux for 30 min, and cooled. Then, 250 ml water was added and the mixture was extracted with three 50-ml ether portions. The extract was subjected to chromatography on an alumina column with 3:1 ether—hexane as the eluent. Most of the solvent was distilled off the eluate and the crystalline precipitate was filtered off. The product was recrystallized from hexane, mp 97°C. PMR spectrum in $CDCl_3$: 7.15 (11H, m, $2C_6H_5$ and 1CH=), 9.95 ppm (1H, s, CH=O). The yield of Va was 5.0 g (45%).

Aldehyde VIb and ketone VIc were analogously synthesized from Vb and Vc, respectively.

2-(Phenyltelluro)-1-cyclohexene-1-carbaldehyde (Vb, $C_{13}H_{14}OTe$) was obtained in 57% yield as yellow crystals, mp 74°C (from hexane). PMR spectrum in $CDCl_3$: 2.35 (8H, m, $4CH_2$), 7.46 (5H, m, C_6H_5), 9.55 ppm (1H, s, CH=O).

1-Phenyl-3-(phenyltelluro)propenone-1 (Vc, $C_{15}H_{12}OTe$) was obtained in 47% yield as bright yellow needles, mp 85°C (from hexane). PMR spectrum in $CDCl_3$: 7.73 (10H, m, $2C_6H_5$), 8.38 (1H, d, J = 8.79 Hz, —CH=), 9.20 ppm (1H, d, J = 8.79 Hz, —CH=).

3-Phenyl-3-(4′-ethoxyphenyltelluro)propenal-1 (Vd, $C_{17}H_{16}O_2Te$). A mixture of 7.46 g (15 mmoles) di(4-ethoxyphenyl) ditelluride, 0.21 g (30 mmoles) lithium, and 0.4 g naphthalene in 30 ml absolute THF was heated at reflux in an argon atmosphere for 3 h. The light yellow solution obtained containing tellurolate anion was added dropwise with stirring to a solution of 4.98 g (30 mmoles) aldehyde VIa in 50 ml THF at −10°C and maintained at this temperature for 30 min. The reaction mixture was then heated at reflux for 30 min and cooled. Then, 250 ml water was added and the mixture was extracted with three 50-ml ether portions. The extract was dried over Na_2SO_4 and the solvent was removed. The residual oil was triturated with hexane to give yellow needles, mp 109°C (from hexane). PMR spectrum in $CDCl_3$: 1.30 (3H, t, CH_3), 3.90 (2H, q, CH_2), 6.48 (2H, d, 3′-,5′-H), 6.98 (5H, m, C_6H_5), 7.25 (2H, d, 2′,6′-H), 7.34 (1H, s, CH=), 9.90 ppm (1H, s, CHO). The yield of Vd was 5.01 g (44%).

Product Ve was analogously synthesized from aldehyde VIb.

2-(4′-Ethoxyphenyltelluro)-1-cyclohexene-1-carbaldehyde (Ve, $C_{15}H_{18}O_2Te$) was obtained in 37% yield as yellow crystals, mp 90°C (from methanol). PMR spectrum in $CDCl_3$: 1.40 (3H, t, CH_3), 2.35 (8H, m, $4CH_2$), 4.01 (2H, q, CH_2), 6.81 (2H, d, 3′-,5′-H), 7.69 (2H, d, 2′,5′-H), 7.69 (2H,6′-H), 9.65 (1H, s, CHO).

2-(Butyltelluro)benzyl Alcohol (IVa, $C_{11}H_{16}OTe$). A. A solution of 9.35 g (50 mmoles) *o*-bromobenzyl alcohol in 10 ml THF was added dropwise with stirring to a solution of phenyllithium obtained from 8.64 g (55 mmoles) bromobenzene and 1.46 g (210 mg-atoms) lithium in 50 ml ether initially at +10°C at a rate such that the temperature did not exceed 10-15°C. A sample of 6.85 g (50 mmoles) butyl bromide was added to the solution of lithium *o*-bromobenzylate with a residue of unreacted lithium cooled initially to 0°C, maintaining the temperature of the mixture at 8-10°C until all the lithium disappeared. After 30-40 min, 6.38 g (50 mmoles) powdered tellurium was added in small portions. The mixture heated spontaneously to reflux. After heating at reflux for 1 h, the solution was cooled and poured into 100 g ice. The ethereal layer was separated and dried over $CaCl_2$. Ether was distilled off and the residue was distilled in vacuum to give IVa as a light yellow oil, bp 175-178°C (2 mm Hg). PMR spectrum in $CDCl_3$: 1.87 (9H, m, C_4H_9), 3.02 (1H, s, OH), 4.64 (2H, s, CH_2OH), 7.40 ppm (4H, m, C_6H_4). The yield of IVa was 12.0-12.4 g (82-85%).

B. A solution of 0.76 g (20 mmoles) sodium borohydride and 0.8 g (20 mmoles) NaOH in 4 ml water was added dropwise with stirring to a solution of 5 g (17.3 mmoles) *o*-(butyltelluro)benzaldehyde in 10 ml ethanol and 5 ml benzene heated to reflux. The mixture was poured into 30 ml water and acidified with hydrochloric acid until slightly acidic. The organic layer was separated, washed with two 10-ml water portions, and dried over Na_2SO_4. The solvent was distilled off and the residue was distilled in vacuum to give 4.6 g (91%) IVa.

Phenyl(2-butyltellurophenyl)methanol (IVb, $C_{17}H_{20}OTe$) and 4-methylphenyl(2-butyltellurophenyl)methanol (IVc, $C_{18}H_{22}OTe$) were synthesized from 2-(butyltelluro)benzaldehyde and phenylmagnesium bromide or 4-methylphenylmagnesium bromide, respectively, and used for oxidation by halogens to give alcohols VIII without separation as pure compounds.

1-(2′-Butyltellurophenyl)-1-ethanol (IVd, $C_{12}H_{18}OTe$) was synthesized analogously in 82% yield starting from methylmagnesium iodide. This compound is a light yellow oil with bp 196-198°C (3 mm Hg). PMR spectrum in CD_2Cl_2: 1.87 (9H, m, C_4H_9), 3.08 (1H, s, OH), 6.08 (1H, s, CHOH), 7.45 ppm (9H, m, C_6H_4 and C_6H_5).

2-Chloro-2-(4-ethoxyphenyl)-3-phenyl-1,2-oxatellurole (Ie, $C_{17}H_{17}ClO_2Te$). A solution of 0.114 g (3 mmoles) sodium borohydride in 10 ml ethanol was added dropwise with stirring to a suspension of 2.0 g (5.2 mmoles) aldehyde Vd in 20 ml methanol at room temperature. The reaction mixture was maintained at room temperature for 30 min and 100 ml saturated aqueous NaCl was added. The mixture was extracted with two 25-ml chloroform portions. The extract was washed with water and dried over Na_2SO_4. A solution of 0.56 g (5.2 mmoles) *tert*-butyl hypochlorite in 5 ml chloroform was added dropwise with stirring to the dry extract at room temperature and maintained for 30 min. The reaction mixture was subjected to chromatography on an alumina column using chloroform as the eluent. The eluate was evaporated and the residual oil was triturated with hexane. The yield of Ie was 1.6 g (75%), mp 130.5°C (from acetone).

Oxatelluroles Ia-Ic were obtained analogously from aldehydes Va-Vc, respectively (see Table 1).

2-Phenyl-2-chloro-1,2-oxatellurole (Id, C_9H_9ClOTe). A sample of 0.61 g (16 mmoles) dry sodium borohydride was added with stirring to a suspension of 3.0 g (7.3 mmoles) diphenyl ditelluride in 30 ml 2-propanol at room temperature. A solution of 0.82 g (14.6 mmoles) propargyl alcohol in 5 ml 2-propanol was added dropwise with stirring to the yellow solution obtained. The mixture was heated at reflux for 1 h, cooled, and treated as described for heterocycle Ie to give 1.9 g (44%) Id, mp 128°C (from methanol).

Heterocycles If and Ig were analogously synthesized from di(4-ethoxyphenyl) ditelluride and di(4-methoxyphenyl) ditelluride, respectively (see Table 1).

2-Iodo-2-(4-ethoxyphenyl)-1,2-oxatellurole (Ii, $C_{11}H_{13}O_2Te$). A mixture of 1.70 g (5 mmoles) heterocycle If and 0.91 g (5.5 mmoles) KI in 15 ml acetone was heated at reflux for 1 h. The mixture was cooled, treated with 50 ml water and extracted with two 15-ml chloroform portions. The extract was evaporated and the residue was crystallized from methanol to give 1.98 g (92%) Ii as lemon yellow crystals, mp 104°C.

Oxatellurole Ih was obtained analogously from Id (see Table 1).

Phenyl(2-butyldichlorotellurophenyl)methanol) (VIIIe, $C_{17}H_{20}Cl_2OTe$). Dry chlorine was passed through a solution of 7.36 g (20 mmoles) alcohol IVb in 50 ml CCl_4 cooled on an ice bath until the solution became colorless. The yellow oil obtained upon evaporation of the solvent in the air was crystallized by trituration with hexane. Recrystallization from 1:1 benzene—hexane gave 5.60 g (64%) tellurium dichloride VIIIe as colorless needles, mp 137-139°C.

Tellurium dichlorides VIIIh and VIIIk were analogously synthesized from alcohols IVc and IVd, respectively (see Table 2). 2-(Butyldichlorotelluro)benzyl alcohol VIIIa was not obtained from IVa in analytically pure form since it undergoes partial dehydrochlorination upon recrystallization.

2-Butyldibromotelluro)benzyl Alcohol (VIIIb, $C_{11}H_{16}Br_2OTe$). A solution of 6.14 g (38.4 mmoles) bromine in 5 ml CCl_4 cooled to −10°C was added dropwise with stirring to a solution of 11.20 g (38.4 mmoles) 2-(butyltelluro)benzyl alcohol IVa in 10 ml CCl_4 at −10°C. The reaction mixture was maintained for 12 h at −10°C. The crystalline precipitate was filtered off and dried to give 14.4 g (83%) VIIIb as lemon yellow crystals, mp 94-96°C (from 1:1:1 CCl_4—ether—hexane).

Tellurium dibromides VIIIf, VIIIi, and VIIIk were analogously obtained from alcohols IVb-IVd, respectively (see Table 2).

2-(Butyldiiodotelluro)benzyl Alcohol (VIIIc, $C_{11}H_{16}I_2OTe$). A sample of 11.7 g (40 mmoles) alcohol IVa was added with stirring to a suspension of 10.2 g (40 mmoles) finely ground iodine in 50 ml ethanol-free chloroform at room temperature and heated on a steam bath until the iodine was completely dissolved. Heating was discontinued and the solvent was evaporated in the air. The red oil formed was crystallized by trituration with petroleum ether to give 13.1 g (60%) VIIIc as red crystals, mp 108-110°C (from 1:2 CCl_4—ether).

Diiodides VIIIg, VIIIj, and VIIIm were obtained analogously from alcohols IVb-IVd, respectively (see Table 2).

1-Butyl-1-chlorobenz-2,1-oxatellurole (IIa, $C_{11}H_{15}ClOTe$). 2-Butyldichlorotelluro)benzyl alcohol VIIIa was synthesized by the oxidation of a solution of 11.7 g (40 mmoles) alcohol IVa in 50 ml CCl_4 by chlorine and subsequent evaporation of the solvent. This alcohol was then dissolved in 200 ml ether. The solution obtained was passed through a 3.5×15-cm alumina column. The product was eluted with 100 ml ether. The eluate was dried over Na_2SO_4. The solvent was distilled off to give 11.6 g (89%) IIa, mp 114-115°C (from 2-propanol).

Benzoxatelluroles IIe, IIh, and IIk were obtained analogously using the corresponding recrystallized tellurium dichlorides VIIIe, VIIIh, and VIIIk (see Table 3).

1-Butyl-1-bromobenz-2,1-oxatellurole (IIb, $C_{11}H_{15}BrOTe$). A sample of 0.56 g (5.5 mmoles) triethylamine was added dropwise with stirring to a solution of 2.44 g (5.4 mmoles) 2-(butyldibromotelluro)benzyl alcohol VIIIb in 10 ml benzene. The mixture became hot and a precipitate of 0.90 g (100%) triethylamine hydrobromide immediately precipitated. This precipitate was filtered off. The filtrate was washed with two 15-ml water portions and evaporated to 4 ml. Then, 6 ml ether and 2 ml hexane were added. The precipitate formed was filtered off and recrystallized from acetonitrile to give 1.56 g (78%) IIb as colorless needles, mp 113-114°C.

Bromides IIf, IIi, and II*l* were obtained analogously from dibromides VIIIf, VIIIi, and VIII*l* (see Table 3).

1-Butyl-1-iodobenz-2,1-oxatellurole (IIc, $C_{11}H_{15}IOTe$). A. Diiodide VIIIc was treated according to the procedure for IIb to give IIc, mp 110-112°C (from acetonitrile). The yield of IIc was 75%.

Iodides IIg, IIj, and IIm were obtained analogously from diiodides VIIIg, VIIIj, and VIIIm, respectively (see Table 3).

B. A sample of 0.70 g (11 mmoles) zinc powder was added to a solution of 3.70 g (10 mmoles) 1-butyl-1-bromobenz-2,1-oxatellurole (IIb) in 50 ml methanol and heated at reflux with stirring for 20-30 min. The zinc was

almost completely dissolved and the solution turned greenish yellow. After cooling, 50 ml chloroform was added and the mixture was washed with three 30-ml water portions. A solution of 1.27 g (5 mmoles) iodine in 20 ml chloroform was added with stirring to the solution obtained at 10-15°C. After stirring for 30 min, the solvent was evaporated and the residue was crystallized from acetonitrile to give 3.0 g (72%) IIc.

1-Butyl-1-fluorobenz-2,1-oxatellurole (IId, $C_{11}H_{15}FOTe$). A mixture of 8.13 g (18 mmoles) dibromide VIIIb in 50 ml $CHCl_3$ and 4.70 g (37 mmoles) AgF, obtained *in situ* by dissolving the calculated amount of Ag_2CO_3 in a mixture of 50 ml water and the calculated amount of 40% hydrofluoric acid, was shaken periodically in a separatory funnel for 30-40 min. The yellow precipitate of AgBr (6.75 g, 100%) was filtered off. The organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was distilled off in vacuum. The residual yellow oil was dissolved in 50 ml ether and passed through an alumina column. The eluate was evaporated to give 4.85 g (87%) fluoride IId as a colorless oil (see Table 3).

1-Phenyl-1-chlorobenz-2,1-oxatellurol-3-one (XIa, $C_{13}H_9ClO_2Te$). A. A sample of 2.52 g (25 mmoles) triethylamine was added with stirring to a hot solution of 10.0 g (25.2 mmoles) 2-carboxyphenyl(phenyl)tellurium dichloride in 50 ml benzene and heated at reflux for 1 h. After cooling, 3.20 g (92%) triethylamine hydrochloride was filtered off. The filtrate was evaporated to half volume and an equal volume of hexane was added. The crystalline precipitate of chloride XIa was filtered off and dried, mp 176.5°C (from 1:1 benzene—hexane). IR spectrum: 1667 cm^{-1} (C=O). The yield of XIa was 8.28 g (92%).

B. A solution of 2.7 g (25 mmoles) *tert*-butyl hypochlorite in 5 ml chloroform was added to a solution of 8.15, (25 mmoles) 2-phenyl(dichlorotelluro)benzoic acid with stirring at room temperature. After stirring for 30 min at the same temperature, the solvent is distilled in vacuum. Oily product XIa was crystallized by trituration with hexane and then recrystallized from benzene—hexane. The yield of XIa was 7.8 g (87%).

1-Chloro-1-(4′-methoxyphenyl)benz-2,1-oxatellurol-3-one (XIb, $C_{14}H_{11}ClO_2Te$) was obtained in 82% yield according to procedure A from 2-carboxyphenyl(4′-methoxyphenyl)tellurium dichloride as colorless crystals, mp 128-129°C (from chloroform—ether). IR spectrum: 1670 cm^{-1}.

1-Chloro-1-(4′-ethoxyphenyl)benz-2,1-oxatellurol-3-one (XIc, $C_{15}H_{13}ClO_2Te$) was obtained in 75% yield similarly to XIa and XIb using procedure A from 2-carboxyphenyl(4′-ethoxyphenyl)tellurium dichloride, mp 113-115°C. IR spectrum: 1668 cm^{-1} (C=O).

Bis(1-butyl-2,1-benzoxatellurol-1-yl) Oxide (IIo, $C_{22}H_{30}O_3Te_2$). A sample of 20.8 g (56 mmoles) heterocycle IIb was added in small portions to a stirred solution of sodium methylate obtained by dissolving 1.35 g (58 mmoles) sodium in 50 ml absolute methanol. Then, 15 ml methanol was distilled off the solution obtained and 1.08 g (60 mmoles) water was added. The mixture was stirred for 15 min and 200 ml ether was added. The precipitate of 5.35 g (52 mmoles) NaBr was filtered off and the solvent was distilled off the filtrate. The oily residue was dissolved in a mixture of 100 ml ether and 50 ml hexane. Traces of NaBr were filtered off and the filtrate was evaporated. The light yellow oily residue was dissolved in a mixture of 75 ml ether and 25 ml hexane and maintained for 24 h at −10°C in order to crystallize IIo, mp 89-91°C. The yield of IIo was 5.35 g (32%).

1-Acetoxy-1-butylbenz-2,1-oxatellurole (IIn, $C_{13}H_{18}O_3Te$). A. A solution of 1.67 g (10 mmoles) $AgOCOCH_3$ in 30 ml methanol was added to a solution of 3.70 g (10 mmoles) bromide IIb in 20 ml methanol. The precipitate of AgBr (1.88 g, 100%) was filtered off and the filtrate was evaporated to 15 ml. Then, 50 ml hexane was added and the mixture was heated at reflux with a Dean—Stark trap to remove methanol completely. The solution of product IIn in hexane was evaporated to 10 ml and maintained at −10°C for 24 h. The solution was filtered and voluminous needles of acetate IIn were dried, mp 69-71°C. The yield of IIn was 1.75 g (50%).

B. A sample of 0.72 g (12 mmoles) acetic acid was added with stirring to a solution of 3.40 g (5.7 mmoles) oxide IIo in 30 ml benzene. The water separated was removed by azeotropic distillation with 20 ml benzene. Slow evaporation of the remaining solvent gave voluminous colorless crystals of IIn, mp 68-71°C. The yield of IIn was 3.80 g (95%).

2-(Butyldibromotelluro)benzaldehyde (XIIa, $C_{11}H_{14}Br_2OTe$). A sample of 1.6 g (10 mmoles) Br_2 was added to a solution of 3.7 g (10 mmoles) bromide IIb in 40 ml CCl_4 and the mixture was heated at reflux for 5 h until the bromine color disappeared and the HBr was no longer liberated. The solution was evaporated to dryness and the oily yellow residue was triturated with petroleum ether to give 4.3 g (95%) XIIIa as lemon yellow needles, mp 150-152°C (from methanol).

2-Butyldibromotelluro)benzophenone (XIIb, $C_{17}H_{18}Br_2OTe$) was obtained analogously in 79% yield from bromide IIf as bright yellow needles, mp 156-158°C (from 1:1 chloroform—hexane).

2-(Tribromotelluro)benzaldehyde (XV, $C_7H_5Br_3OTe$). A sample of 13.54 g (84.6 mmoles) Br_2 was added to a solution of 15.7 g (42.3 mmoles) bromide IIb in 50 ml glacial acetic acid at 50°C and the mixture obtained was heated at

reflux. Aldehyde XV precipitated after 10 min as fine golden flakes. The mixture was cooled and diluted with an equal volume of ether. The precipitate was filtered off and dried. The yield of XV was 12.6 g (63%), mp 228-230°C.

A sample of 12 g (25.4 mmoles) aldehyde XV was reduced with aqueous sodium metabisulfite according to a reported procedure [21] to give 5.6 g (94%) ditellurodisalicylaldehyde, mp 158-160°C.

2-Butyldibromotelluro-ω,ω-dibromoacetophenone (XIIIe, $C_{12}H_{14}Br_4OTe$). A solution of 3.86 g (10 mmoles) bromide IIb in 10 ml CCl_4 was added dropwise to a solution of 3.2 g (20 mmoles) Br_2 in 50 ml CCl_4 at reflux. The mixture was heated at reflux for 10 min until a precipitate formed and the bromine color disappeared. Then, the mixture was evaporated to dryness and the residue was recrystallized four or five times from benzene to give 2.24 g (36%) yellow crystalline XIIIe, mp 162-165°C.

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