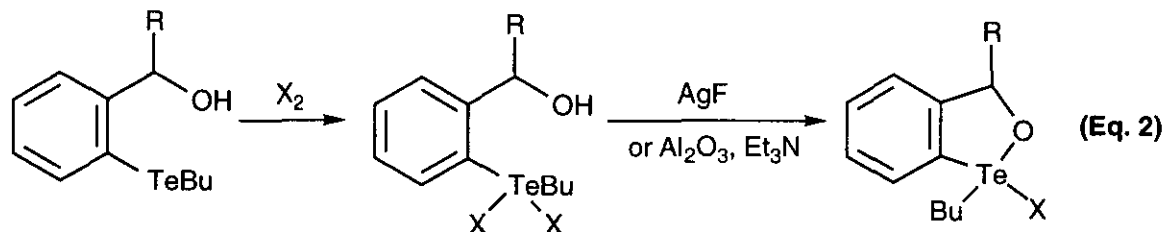


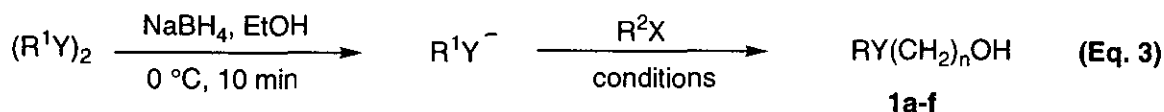


purity.<sup>1a,c</sup> In contrast to halooxasulfuranes and halooxaselenuranes, studies on the chemistry of analogous cyclic halooxatelluranes (**A**: **Y** = **Te**) have received much less attention.<sup>2</sup>

Some Russian scientists have reported the first example of halooxatellurane in 1993<sup>3a,b</sup> and very recently they also reported the synthetic application of 3*H* (3*R*)-benzo-2,1-oxatelluroles as a synthon for *O*-alkyltellurophenyl carbonyl compounds.<sup>3c,d</sup> They prepared the telluroles by oxidation of tellurides having hydroxy group at  $\gamma$  position with halogens followed by dehydrohalogenation with AgF or Al<sub>2</sub>O<sub>3</sub> and Et<sub>3</sub>N (Eq. 2).



Considering both strong reducing ability and halophilicity of the tellurides, we expected that cyclic halooxatelluranes would be more stable, and more readily available than its sulfur and selenium analogs. Hence the reaction of tellurides (**B**: **Y** = **Te**) with active halo compounds in place of strong halogenation reagents (X<sup>+</sup>) should provide a simple way for synthesis of cyclic halooxatelluranes.<sup>4</sup> Here we report the results on the synthesis of simple halooxatelluranes (**3a**, **4a-d**, **5a**) from tellurides (**1a-d**) via dehalogenation of  $\alpha$ -halo



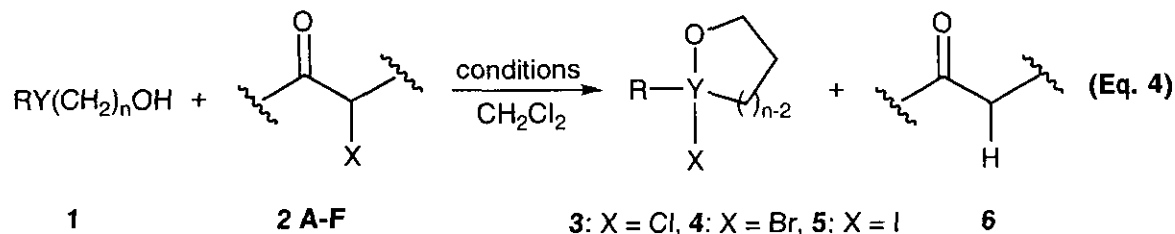
**a**: R = Me, Y = Te, n = 3   **b**: R = Et, Y = Te, n = 3  
**c**: R = Et, Y = Te, n = 4   **d**: R = Ph, Y = Te, n = 3  
**e**: R = Et, Y = Se, n = 3   **f**: R = Ph, Y = Se, n = 3

$(R^1Y)_2$	$R^2X$	conditions	$RY(CH_2)_nOH$	yield (%)
(MeTe) <sub>2</sub>	HO(CH <sub>2</sub> ) <sub>3</sub> Br	rt, 1.5 h	<b>1a</b>	76
(EtTe) <sub>2</sub>	HO(CH <sub>2</sub> ) <sub>3</sub> Br	rt, 1.5 h	<b>1b</b>	66
[HO(CH <sub>2</sub> ) <sub>3</sub> Te] <sub>2</sub>	EtBr	rt, 1.5 h	<b>1b</b>	82
[HO(CH <sub>2</sub> ) <sub>4</sub> Te] <sub>2</sub>	EtBr	rt, 1.5 h	<b>1c</b>	81
(PhTe) <sub>2</sub>	HO(CH <sub>2</sub> ) <sub>3</sub> Br	reflux, 4 h	<b>1d</b>	61

**Table 1. Synthesis of tellurides (1a-d).**

carbonyl compounds (2A-F).

Tellurides (1a-d) were readily prepared as shown in Eq.3. Reduction of ditellurides<sup>5</sup> with NaBH<sub>4</sub> in EtOH at 0 ° C followed by treatment with appropriate alkyl halide at room temperature or under refluxing gave tellurides (1a-d) in yield as shown in Table 1. Tellurides without hydroxy group on the side chain are known to react with α-halo carbonyl compounds to give telluronium salts which were used in the Wittig type reaction and cyclopropanation.<sup>6</sup> Unexpectedly, when the telluride (1b) reacted with phenacyl bromide



a: R = Me, Y = Te, n = 3    b: R = Et, Y = Te, n = 3  
 c: R = Et, Y = Te, n = 4    d: R = Ph, Y = Te, n = 3  
 e: R = Et, Y = Se, n = 3    f: R = Ph, Y = Se, n = 3

entry	RY(CH <sub>2</sub> ) <sub>n</sub> OH	2A-F	conditions	yield of 3-5	yield of 6
1	1a	2A	reflux, 8 h	3a 86	6a 90
2	1a	2B	rt, 2.5 h	4a 79	6a 99
3	1a	2C	rt, 1.5 h	5a 53	6a 98
4	1a	2D	rt, 2.5 h	4a 72	6b 96
5	1b	2B	rt, 2.5 h	4b 87	6a 95
6	1b	2E	rt, 2h	4b 71	6c 95
7	1b	2F	rt, 2 h	4b 71	6d 95
8	1c	2B	rt, 2.5 h	4c 51	6a 92
9	1c	2D	rt, 2 h	4c 63	6b 97
10	1d	2B	rt, 5.5 h	4d 71	6a 97

**Table 2: Preparation of halooxatelluranes (3-5) via dehalogenation of α-halo carbonyl compounds (2A-F) with tellurides (1a-d).**

2A-F: A = phenacyl chloride, B = phenacyl bromide, C = phenacyl iodide, D = 4-bromophenacyl bromide, E = diethyl bromomalonate, F = diethyl dibromomalonate.

6a-d: a = acetophenone, b = 4'-bromoacetophenone, c = diethyl malonate, d = diethyl bromomalonate

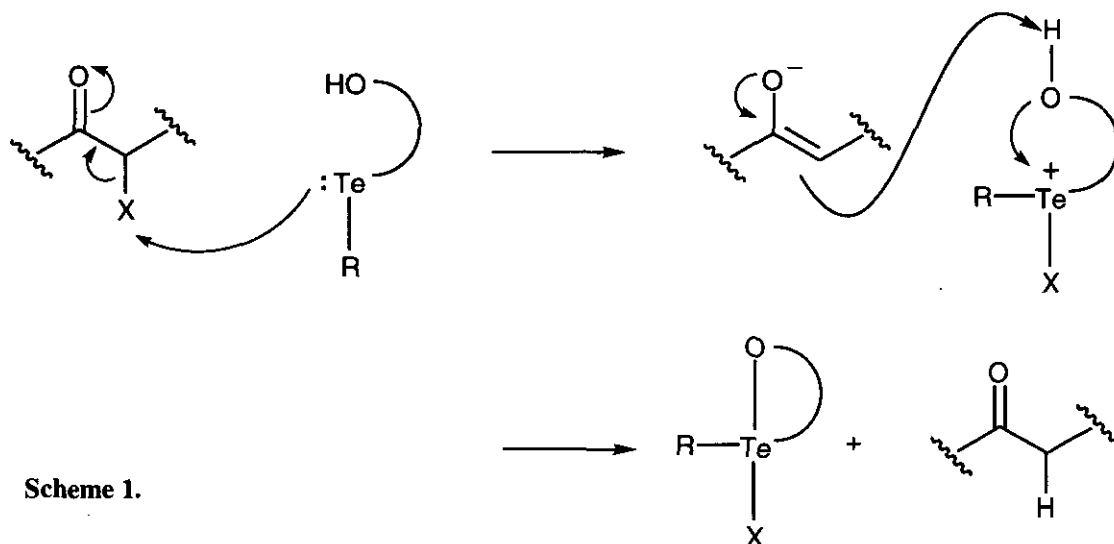
(**2B**) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 2.5 h, debromination occurred to give bromotellurane (**4b**) in good yield, instead of the formation of telluronium salt.<sup>7</sup> This result suggested that halooxatelluranes could be synthesized from telluride having hydroxy group on the side chain by dehalogenation of  $\alpha$ -halo carbonyl compounds. We thus set out to investigate the generality of this reaction with several model compounds. Reaction of telluride (**1a**) with phenacyl bromide (**2B**) or 4-bromophenacyl bromide (**2D**) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 2.5 h gave bromooxatellurane (**4a**) in good yield, respectively (Table 2). Reaction of **1a** with phenacyl iodide (**2C**) was completed at room temperature within 1.5 h, while that with phenacyl chloride (**2A**) required 8 h-refluxing in  $\text{CH}_2\text{Cl}_2$ . Therefore, the reactivity of  $\alpha$ -halo carbonyl compounds in this reaction is in the order: iodide, bromide and chloride. Prolonging the hydroxypolymethylene chain from three carbons to four carbons in the tellurides showed little effect on their reactivity (entries 8 and 9 in Table 2). Reaction of the telluride (**1d**) with phenacyl bromide (**2B**) required 5.5 h to complete, indicating that **1d** has slightly lower reactivity compared with that of **1a-c**. These results would be explained by the electron withdrawing effect of phenyl group. In addition, treatment of tellurides (**1a-d**) with other active halo compounds such as diethyl bromomalonate (**2E**) and diethyl dibromomalonate (**2F**) also provided the bromooxatelluranes in good yields (Eq. 4, Table 2).

In order to compare the halophilic reactivity of the tellurides with that of the corresponding selenides, similar reactions were examined with selenides (**1e, f**).<sup>7</sup> No product was detected when selenides (**1e, f**) reacted with phenacyl bromide (**2B**) in  $\text{CH}_2\text{Cl}_2$  at room temperature. After a solution of selenide (**1e**) and diethyl dibromomalonate (**2F**) in  $\text{CH}_2\text{Cl}_2$  was refluxed for 24 h, 50% of the selenide (**1e**) was converted into bromooxaselenurane (**4e**). Only about 5% of the bromooxaselenurane (**4e**) was obtained even after the selenide (**1e**) and diethyl bromomalonate (**2E**) were refluxed in benzene for 13 h.

The reaction showed noteworthy characteristic of its simplicity. Reactions were usually performed in  $\text{CH}_2\text{Cl}_2$  at room temperature and were readily monitored by TLC. No any side reaction or by-product was detected. After the reaction completed, only evaporation of the solvent was needed to give product mixtures, which were easily separated by column chromatography for the large different polarity between dehalogenation products (**6**) and halooxatelluranes (**3-5**) usually hexane / EtOAc (9:1) system afforded dehalogenation compounds and  $\text{CHCl}_3$  / MeOH (9:1) system gave halooxatelluranes.

Although the detailed mechanism of the reaction is not clear at the present time, the reaction may take place by the attack of the tellurium lone pair on the halogen atom followed by deprotonation and intramolecular cyclization as shown in Scheme 1.<sup>2,4,8</sup>

In conclusion, telluride has been proved to be more halophilic compared with the corresponding sulfide and



selenide: therefore, tellurides containing hydroxy group on the side chain have been readily converted into cyclic halooxatelluranes by dehalogenation of  $\alpha$ -halo carbonyl compounds. By replacement of the oxygen atom on the side chain with other heteroatoms, the novel heteroatom containing hypervalent cyclic tellurane could also be prepared in this mild way. We consider this is a convenient and general method for the synthesis of tellurium-containing heterocyclic compounds.

## EXPERIMENTAL

Melting points were taken with a Yanaco micromelting point apparatus and are uncorrected. Spectroscopic measurements were carried out with the following instruments: IR, Perkin-Elmer 1600 Series FTIR; mass (MS) and high resolution mass spectra (HRMS), JMS-AX 505H;  $^1\text{H-NMR}$ , Varian Gemini-300 (300 MHz) for solutions in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as an internal standard,  $J$  values in Hz. The chemical shifts from  $\text{Me}_4\text{Si}$  were calculated based on  $\text{CDCl}_3$ . All reactions were carried out in dried glassware under  $\text{N}_2$  atmosphere. Dry  $\text{CH}_2\text{Cl}_2$  was distilled over  $\text{P}_2\text{O}_5$  and stored over  $4\text{\AA}$  molecular sieves. Column chromatography and TLC were performed on Kiesel gel 60 (Merck, Art. 7734 and Art. 5715, respectively).

**Dimethyl ditelluride:** The ditelluride was synthesized according to the procedure reported in the literature.<sup>5</sup> From tellurium powder (2.56 g, 20 mmol) and dimethyl sulfate (2.0 mL, 21 mmol) was obtained dimethyl ditelluride (1.7 g, 59%) as a red oil.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 2.67 (6H, s).

**Diethyl ditelluride:** From tellurium powder (2.56 g, 20 mmol) and ethyl bromide (2.0 mL, 26.79 mmol) was obtained diethyl ditelluride (2.46 g, 78%) as a red oil.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.62 (6H, t,  $J = 7.7$ ), 3.04 (4H, q,  $J = 7.7$ ).

**Di-(3-hydroxy)propyl ditelluride:** From tellurium powder (2.56 g, 20 mmol) and 3-bromo-1-propanol (2.0 mL, 22.22 mmol) was obtained di-(3-hydroxy)propyl ditelluride (3.15 g, 84%) as a red oil. bp: 162° C at 0.9 mmHg. IR  $\nu_{\max}$  (neat)  $\text{cm}^{-1}$ : 3316, 2926, 1425, 1150, 1048, 670.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.60 (2H, br), 2.00 (4H, tt,  $J = 6.0, 7.1$ ), 3.18 (4H, t,  $J = 7.1$ ), 3.71 (4H, t,  $J = 6.0$ ). MS  $m/z$ : 378 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ,  $^{130}\text{Te}$ ), 376 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ,  $^{128}\text{Te}$ ), 374 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ,  $^{128}\text{Te}$  or  $^{130}\text{Te}$ ,  $^{126}\text{Te}$ ), 372 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ,  $^{126}\text{Te}$ ), 370 ( $\text{M}^+$ ,  $^{126}\text{Te}$ ,  $^{126}\text{Te}$ ), 317, 315, 313, 260, 258, 256, 254, 252, 188, 186, 184, 130, 128, 126, 59. HRMS: Calcd for  $\text{C}_6\text{H}_{14}\text{O}_2\text{Te}_2$ : 377.9132 ( $^{130}\text{Te}$ ,  $^{130}\text{Te}$ ), 373.9104 ( $^{128}\text{Te}$ ,  $^{128}\text{Te}$ ). Found: 377.9148 ( $^{130}\text{Te}$ ,  $^{130}\text{Te}$ ), 373.9099 ( $^{128}\text{Te}$ ,  $^{128}\text{Te}$ ).

**Di-(4-hydroxy)butyl ditelluride:** From tellurium powder (2.56 g, 20 mmol) and 4-chloro-1-butanol (2.2 mL, 22.09 mmol) was obtained di-(4-hydroxy)butyl ditelluride (3.12 g, 78%) as a red oil. bp: 116° C at 0.5 mmHg. IR  $\nu_{\max}$  (neat)  $\text{cm}^{-1}$ : 3329, 2926, 1448, 1055, 910.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.6-1.8 (6H, m), 1.8-1.95 (4H, m), 3.11 (4H, t,  $J = 7.4$ ), 3.68 (4H, t,  $J = 6.3$ ). MS  $m/z$ : 406 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ,  $^{130}\text{Te}$ ), 404 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ,  $^{128}\text{Te}$ ), 402 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ,  $^{128}\text{Te}$  or  $^{130}\text{Te}$ ,  $^{126}\text{Te}$ ), 400 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ,  $^{126}\text{Te}$ ), 398 ( $\text{M}^+$ ,  $^{126}\text{Te}$ ,  $^{126}\text{Te}$ ), 334, 332, 330, 316, 314, 312, 310, 308, 260, 258, 256, 254, 252, 202, 200, 198, 130, 128, 126, 91, 73, 55. HRMS: Calcd for  $\text{C}_8\text{H}_{18}\text{O}_2\text{Te}_2$ : 405.9445 ( $^{130}\text{Te}$ ,  $^{130}\text{Te}$ ), 401.9417 ( $^{128}\text{Te}$ ,  $^{128}\text{Te}$ ). Found: 405.9475 ( $^{130}\text{Te}$ ,  $^{130}\text{Te}$ ), 401.9407 ( $^{128}\text{Te}$ ,  $^{128}\text{Te}$ ).

**Di-(3-hydroxy)propyl diselenide:** Diselenide was synthesized according to the method reported in the literature.<sup>7</sup> From selenium (2.0 g, 25 mmol), powdered sodium hydroxide (1.5 g, 38 mmol), hydrazine hydrate (0.35 mL, 7 mmol) and 3-bromo-1-propanol (2.3 mL, 26 mmol) was obtained di-(3-hydroxy)propyl diselenide (2.62 g, 76%) as a yellow oil. IR  $\nu_{\max}$  (neat)  $\text{cm}^{-1}$ : 3343, 2930, 1388, 1053, 887.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.7-1.8 (2H, br), 2.01 (4H, tt,  $J = 6.0, 7.0$ ), 3.03 (4H, t,  $J = 7.1$ ), 3.76 (4H, t,  $J = 6.0$ ). MS  $m/z$ : 278 ( $\text{M}^+$ ,  $^{80}\text{Se}$ ,  $^{80}\text{Se}$ ), 276 ( $\text{M}^+$ ,  $^{80}\text{Se}$ ,  $^{78}\text{Se}$ ), 274 ( $\text{M}^+$ ,  $^{78}\text{Se}$ ,  $^{78}\text{Se}$ ), 202, 200, 198, 137, 135, 122, 93, 59, 57. HRMS: Calcd for  $\text{C}_6\text{H}_{14}\text{Se}_2\text{O}_2$ : 277.9322 ( $^{80}\text{Se}$ ,  $^{80}\text{Se}$ ), 273.9341 ( $^{78}\text{Se}$ ,  $^{78}\text{Se}$ ). Found: 277.9301 ( $^{80}\text{Se}$ ,  $^{80}\text{Se}$ ), 273.9339 ( $^{78}\text{Se}$ ,  $^{78}\text{Se}$ ).

**Synthesis of 3-Methyltelluro-1-propanol (1a)** To a solution of dimethyl ditelluride (2.17 g, 7.59 mmol) in abs. EtOH (35 mL) was added  $\text{NaBH}_4$  (650 mg, 17.11 mmol) under  $\text{N}_2$  atmosphere at 0° C, the mixture was stirred until red color of the ditelluride disappeared (ca. 10 min). Then 3-bromo-1-propanol (1.37 mL, 15.24 mmol) was added dropwise to the mixture at 0° C and the whole solution was stirred at rt for 1.5 h. The reaction was quenched with  $\text{H}_2\text{O}$  (10 mL) and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (40 mL x 3). The organic layer was washed with saturated  $\text{NH}_4\text{Cl}$  (6 mL x 1),  $\text{H}_2\text{O}$  (10 mL x 1) followed by brine (10 mL x 1) and dried over  $\text{MgSO}_4$ . Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane / EtOAc 4:1) to give 3-methyltelluro-1-propanol (**1a**) (2.32 g, 76%) as a red oil. bp: 51° C at 0.2 mmHg. IR  $\nu_{\max}$  (neat)  $\text{cm}^{-1}$ : 3328, 2922, 1418, 1219, 1159, 1044, 996.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.60-1.62 (1H, br), 1.91 (3H, s), 2.04 (2H, tt,  $J = 6.0, 7.1$ ), 2.69 (2H, t,  $J = 7.1$ ), 3.71 (2H, t,  $J = 6.0$ ). MS  $m/z$ : 203 ( $\text{M}^+-1$ ,  $^{130}\text{Te}$ ), 201 ( $\text{M}^+-1$ ,  $^{128}\text{Te}$ ), 199 ( $\text{M}^+-1$ ,  $^{126}\text{Te}$ ), 188, 186, 184, 145, 143, 141, 130, 128,

126, 71, 57. HRMS: Calcd for  $C_4H_{10}OTe$ : 203.9801 ( $^{130}Te$ ), 201.9787 ( $^{128}Te$ ). Found: 203.9817 ( $^{130}Te$ ), 201.9751 ( $^{128}Te$ ). 3-Ethyltelluro-1-propanol (**1b**), 4-ethyltelluro-1-butanol (**1c**), and 3-phenyltelluro-1-propanol (**1d**) were prepared similarly.

**3-Ethyltelluro-1-propanol (1b)**: From diethyl ditelluride (320 mg, 1.02 mmol),  $NaBH_4$  (120 mg, 3.16 mmol), and 3-bromo-1-propanol (0.19 mL, 2.1 mmol) or from di-(3-hydroxy)propyl ditelluride (294 mg, 0.79 mmol),  $NaBH_4$  (60 mg, 1.58 mmol), and ethyl bromide (0.15 mL, 1.67 mmol) was obtained 3-ethyltelluro-1-propanol (291 mg, 66% or 275 mg, 81%) as a red oil. bp: 74° C at 1 mmHg. IR  $\nu_{max}$  (neat)  $cm^{-1}$ : 3327, 2925, 1445, 1373, 1196, 1157, 1043, 870.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$ : 1.4-1.5 (1H, br), 1.62 (3H, t,  $J = 7.7$ ), 2.02 (2H, tt,  $J = 6.0, 7.1$ ), 2.65 (2H, q,  $J = 7.7$ ), 2.72 (2H, t,  $J = 7.1$ ), 3.70 (2H, t,  $J = 6.0$ ). MS  $m/z$ : 218 ( $M^+$ ,  $^{130}Te$ ), 216 ( $M^+$ ,  $^{128}Te$ ), 214 ( $M^+$ ,  $^{126}Te$ ), 189, 187, 185, 130, 128, 71, 55. HRMS: Calcd for  $C_5H_{12}OTe$ : 217.9957 ( $^{130}Te$ ), 215.9943 ( $^{128}Te$ ). Found: 217.9927 ( $^{130}Te$ ), 215.9919 ( $^{128}Te$ ).

**4-Ethyltelluro-1-butanol (1c)**: From di-(4-hydroxy)butyl ditelluride (3.07 g, 7.64 mmol),  $NaBH_4$  (580 mg, 15.26 mmol), and ethyl bromide (1.2 mL, 16 mmol) was obtained 4-ethyltelluro-1-butanol (2.85 g, 81%) as a red oil. bp: 69° C at 0.2 mmHg. IR  $\nu_{max}$  (neat)  $cm^{-1}$ : 3328, 2926, 1447, 1374, 1194, 1057, 912.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$ : 1.38-1.41 (1H, br), 1.6-1.75 (5H, m), 1.8-1.9 (2H, m), 2.6-2.75 (4H, m), 3.70 (2H, t,  $J = 6.0$ ). MS  $m/z$ : 232 ( $M^+$ ,  $^{130}Te$ ), 230 ( $M^+$ ,  $^{128}Te$ ), 228 ( $M^+$ ,  $^{126}Te$ ), 185, 183, 181, 130, 128, 126, 73, 55. HRMS: Calcd for  $C_6H_{14}OTe$ : 232.0113 ( $^{130}Te$ ), 230.0099 ( $^{128}Te$ ). Found: 232.0063 ( $^{130}Te$ ), 230.0040 ( $^{128}Te$ ).

**3-Phenyltelluro-1-propanol (1d)**: From diphenyl ditelluride (507 mg, 1.31 mmol),  $NaBH_4$  (150 mg, 3.95 mmol), and 3-bromo-1-propanol (0.24 mL, 2.61 mmol) was obtained 3-phenyltelluro-1-propanol (422 mg, 61%) as a red oil by refluxing in EtOH (10 mL) for 4 h. bp: 92° C at 0.2 mmHg. IR  $\nu_{max}$  (neat)  $cm^{-1}$ : 3341, 2934, 1574, 1474, 1433, 1048, 731.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$ : 1.55-1.6 (1H, br), 2.0-2.15 (2H, m), 2.97 (2H, t,  $J = 7.1$ ), 3.70 (2H, t,  $J = 6.0$ ), 7.2-7.3 (3H, m), 7.7-7.75 (2H, m). MS  $m/z$ : 266 ( $M^+$ ,  $^{130}Te$ ), 264 ( $M^+$ ,  $^{128}Te$ ), 262 ( $M^+$ ,  $^{126}Te$ ), 208, 206, 204, 130, 128, 126, 78, 77, 51. HRMS: Calcd for  $C_9H_{12}OTe$ : 265.9957 ( $^{130}Te$ ), 263.9943 ( $^{128}Te$ ). Found: 265.9968 ( $^{130}Te$ ), 263.9940 ( $^{128}Te$ ).

**3-Ethylselenuro-1-propanol (1e)** To a solution of di-(3-hydroxypropyl) diselenide (1.24 g, 4.49 mmol) in abs. EtOH (25 mL) was added  $NaBH_4$  (341 mg, 8.97 mmol) under  $N_2$  atmosphere at 0 ° C. After the mixture was stirred for 10 min, ethyl bromide (1.0 mL, 13.33 mmol) was added dropwise to the mixture at 0 ° C and the whole solution was stirred at rt for 30 min. The reaction was quenched with  $H_2O$  (6 mL) and the mixture was extracted with  $CH_2Cl_2$  (35 mL x 3). The organic layer was washed with saturated  $NH_4Cl$  (5 mL x 1),  $H_2O$  (10 mL x 1) followed by brine (10 mL x 1) and dried over  $MgSO_4$ . Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane / EtOAc 4:1) to afford pure 3-ethylselenuro-1-propanol (0.92 g, 61%) as a colorless oil. IR  $\nu_{max}$  (neat)  $cm^{-1}$ : 3352, 2924, 1449,

1375, 1231, 1051, 888.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.40 (3H, t,  $J = 7.7$ ), 1.6-1.65 (1H, br), 1.93 (2H, tt,  $J = 6.0, 7.1$ ), 2.59 (2H, q,  $J = 7.7$ ), 2.67 (2H, t,  $J = 7.1$ ), 3.75 (2H, t,  $J = 6.0$ ). MS  $m/z$ : 168 ( $\text{M}^+$ ,  $^{80}\text{Se}$ ), 167 ( $\text{M}^+-1$ ,  $^{80}\text{Se}$ , or  $\text{M}^++1$ ,  $^{78}\text{Se}$ ), 166 ( $\text{M}^+$ ,  $^{78}\text{Se}$ ), 137, 135, 110, 108, 87, 57. HRMS: Calcd for  $\text{C}_3\text{H}_{12}\text{OSe}$ : 168.0052 ( $^{80}\text{Se}$ ), 166.0061 ( $^{78}\text{Se}$ ). Found: 168.0035 ( $^{80}\text{Se}$ ), 166.0053 ( $^{78}\text{Se}$ ).

**3-Phenylselenuro-1-propanol (1f)** To a solution of diphenyl diselenide (3.16 g, 10.13 mmol) in abs. EtOH (100 mL) was added  $\text{NaBH}_4$  (1.12 g, 29.47 mmol) under  $\text{N}_2$  atmosphere at  $0^\circ\text{C}$ . After the mixture was stirred for 10 min, 3-bromo-1-propanol (1.84 mL, 20.44 mmol) was added dropwise to the mixture at  $0^\circ\text{C}$  and the whole solution was stirred at rt overnight. The reaction was quenched with  $\text{H}_2\text{O}$  (10 mL) and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL x 3). The organic layer was washed with saturated  $\text{NH}_4\text{Cl}$  (15 mL x 1),  $\text{H}_2\text{O}$  (15 mL x 1) followed by brine (15 mL x 1) and dried over  $\text{MgSO}_4$ . Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane / EtOAc 4:1) to give 3-phenylselenuro-1-propanol (4.06 g, 93%) as a colorless oil. IR  $\nu_{\text{max}}$  (neat)  $\text{cm}^{-1}$ : 3342, 2937, 1578, 1478, 1437, 1250, 1022, 735, 691.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.4-1.5 (1H, br), 1.95 (2H, tt,  $J = 6.0, 7.1$ ), 3.02 (2H, t,  $J = 7.1$ ), 3.75 (2H, t,  $J = 6.0$ ), 7.25-7.3 (3H, m), 7.5-7.55 (2H, m). MS  $m/z$ : 216 ( $\text{M}^+$ ,  $^{80}\text{Se}$ ), 214 ( $\text{M}^+$ ,  $^{78}\text{Se}$ ), 185, 183, 161, 159, 91, 78, 77, 57, 51. HRMS: Calcd for  $\text{C}_9\text{H}_{12}\text{OSe}$ : 216.0052 ( $^{80}\text{Se}$ ), 214.0061 ( $^{78}\text{Se}$ ). Found: 216.0042 ( $^{80}\text{Se}$ ), 214.0067 ( $^{78}\text{Se}$ ).

**General Procedure for Synthesis of Halooxatelluranes (3a, 4a-d, 5a) and Halooxaselenuranes (4e) via Dehalogenation** A solution of telluride or selenide (0.1-1.2 mmol) and  $\alpha$ -halo carbonyl compound (0.1-1.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (ca. 20 mL for 1 mmol telluride) was stirred at rt (or under refluxing) under argon atmosphere for appropriate time as shown in Table 2. Removal of the solvent under reduced pressure gave the crude product which was chromatographed on silica gel. Elution with hexane / AcOEt (9 : 1) afforded carbonyl compound (6a-d), further elution with  $\text{CHCl}_3$  / MeOH (9 : 1) gave halooxatelluranes (3a, 4a-d, 5a) and halooxaselenuranes (4e) in yields shown in Table 2.

**2-Chloro-2-methyl-1,2-oxatellurolane (3a)**: white solid. mp:  $91^\circ\text{C}$  (decomp). IR  $\nu_{\text{max}}$  (KBr)  $\text{cm}^{-1}$ : 2928, 1403, 1031, 980, 666.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.8-2.0 (1H, m), 2.2-2.3 (1H, m), 2.72 (3H, s), 3.45-3.6 (1H, m), 3.65-3.75 (1H, m), 3.95-4.1 (1H, m), 4.65-4.7 (1H, m). MS  $m/z$ : 203 ( $^{130}\text{Te}$ ,  $\text{M}^+-\text{Cl}$ ), 201 ( $^{128}\text{Te}$ ,  $\text{M}^+-\text{Cl}$ ), 199 ( $^{126}\text{Te}$ ,  $\text{M}^+-\text{Cl}$ ), 188, 186, 184, 130, 128, 126, 105, 77, 57. HRMS: Calcd for  $\text{C}_4\text{H}_9\text{OTe}$  ( $\text{M}^+-\text{Cl}$ ): 202.9722 ( $^{130}\text{Te}$ ), 200.9708 ( $^{128}\text{Te}$ ). found: 202.9704 ( $^{130}\text{Te}$ ), 200.9712 ( $^{128}\text{Te}$ )

**2-Bromo-2-methyl-1,2-oxatellurolane (4a)**: white solid. mp:  $63^\circ\text{C}$  (decomp). IR  $\nu_{\text{max}}$  (KBr)  $\text{cm}^{-1}$ : 2926, 1448, 1407, 1034, 973, 691.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.9-1.95 (1H, m), 2.15-2.25 (1H, m), 2.85 (3H, s), 3.6-3.8 (1H, m), 3.8-3.85 (1H, m), 4.05-4.15 (1H, m), 4.7-4.8 (1H, m). MS  $m/z$ : 203 ( $\text{M}^+-\text{Br}$ ,  $^{130}\text{Te}$ ), 201 ( $\text{M}^+-\text{Br}$ ,  $^{128}\text{Te}$ ),



199 (M<sup>+</sup>-Br, <sup>126</sup>Te), 188, 186, 184, 105, 77, 57. HRMS: Calcd for C<sub>5</sub>H<sub>9</sub>OTe (M<sup>+</sup>-Br): 202.9722 (<sup>130</sup>Te), 200.9708 (<sup>128</sup>Te). Found: 202.9711 (<sup>130</sup>Te), 200.9721 (<sup>128</sup>Te).

**2-Bromo-2-ethyl-1,2-oxatellurolane (4b):** white solid. mp: 102° C (decomp). IR  $\nu_{\max}$  (KBr) cm<sup>-1</sup>: 2930, 1448, 1409, 1033, 997, 969. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.71 (3H, t, *J* = 7.7), 1.85-2.0 (1H, m), 2.1-2.2 (1H, m), 3.2-3.35 (2H, m), 3.55-3.65 (1H, m), 3.7-3.75 (1H, m), 4.07 (1H, dt, *J* = 3.9, 9.9), 4.65-4.7 (1H, m). MS *m/z*: 217 (M<sup>+</sup>-Br, <sup>130</sup>Te), 215 (M<sup>+</sup>-Br, <sup>128</sup>Te), 213 (M<sup>+</sup>-Br, <sup>126</sup>Te), 187, 185, 183, 130, 128, 126, 57. HRMS: Calcd for C<sub>5</sub>H<sub>11</sub>OTe (M<sup>+</sup>-Br): 216.9879 (<sup>130</sup>Te), 214.9865 (<sup>128</sup>Te). Found: 216.9853 (<sup>130</sup>Te), 214.9877 (<sup>128</sup>Te).

**2-Bromo-2-ethyl-1,2-oxatellurane (4c):** colorless oil. IR  $\nu_{\max}$  (neat) cm<sup>-1</sup>: 2931, 1447, 1404, 1024, 908, 752. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.65-1.75 (2H, m), 1.86 (3H, t, *J* = 7.7), 2.2-2.35 (2H, m), 3.38 (2H, q, *J* = 7.7), 3.45-3.5 (1H, m), 3.6-3.7 (1H, m), 3.7-3.8 (2H, m). MS *m/z*: 231 (M<sup>+</sup>-Br, <sup>130</sup>Te), 229 (M<sup>+</sup>-Br, <sup>128</sup>Te), 227 (M<sup>+</sup>-Br, <sup>126</sup>Te), 202, 200, 198, 130, 128, 126, 71, 55. HRMS: Calcd for C<sub>6</sub>H<sub>13</sub>OTe (M<sup>+</sup>-Br): 231.0035 (<sup>130</sup>Te), 229.0021 (<sup>128</sup>Te). Found: 230.9979 (<sup>130</sup>Te), 229.0039 (<sup>128</sup>Te).

**2-Bromo-2-phenyl-1,2-oxatellurolane (4d):** white solid. mp: 153° C (decomp). IR  $\nu_{\max}$  (KBr) cm<sup>-1</sup>: 3432, 2851, 1436, 1028, 966, 732. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.9-2.0 (1H, m), 2.1-2.2 (1H, m), 3.6-3.75 (2H, m), 3.8-3.9 (1H, m), 4.85-4.9 (1H, m), 7.45-7.55 (3H, m), 8.15-8.2 (2H, m). MS *m/z*: 265 (M<sup>+</sup>-Br, <sup>130</sup>Te), 263 (M<sup>+</sup>-Br, <sup>128</sup>Te), 261 (M<sup>+</sup>-Br, <sup>126</sup>Te), 207, 205, 203, 104, 93. HRMS: Calcd for C<sub>9</sub>H<sub>11</sub>OTe (M<sup>+</sup>-Br): 264.9879 (<sup>130</sup>Te), 262.9865 (<sup>128</sup>Te). Found: 264.9858 (<sup>130</sup>Te), 262.9826 (<sup>128</sup>Te).

**2-Bromo-2-ethyl-1,2-oxaselenurolane (4e):** colorless crystal. mp: 104° C (decomp). IR  $\nu_{\max}$  (KBr) cm<sup>-1</sup>: 2943, 1448, 1409, 1235, 959, 869. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.70 (3H, t, *J* = 7.6), 2.15-2.3 (2H, m), 3.45-3.55 (1H, m), 3.95-4.1 (2H, m), 4.25-4.4 (2H, m), 4.5-4.6 (1H, m). MS *m/z*: 167 (M<sup>+</sup>-Br, <sup>80</sup>Se), 165 (M<sup>+</sup>-Br, <sup>78</sup>Se), 139, 137, 109, 107, 82, 80, 57. HRMS: Calcd for C<sub>5</sub>H<sub>11</sub>OSe (M<sup>+</sup>-Br): 166.9974 (<sup>80</sup>Se), 164.9983 (<sup>78</sup>Se). Found: 166.9925 (<sup>80</sup>Se), 164.9920 (<sup>78</sup>Se).

**2-Iodo-2-methyl-1,2-oxatellurolane (5a):** red oil. IR  $\nu_{\max}$  (neat) cm<sup>-1</sup>: 2922, 1403, 1033, 970. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.9-1.95 (1H, m), 2.15-2.4 (1H, m), 3.02 (3H, s), 3.8-3.9 (1H, m), 3.9-4.0 (1H, m), 4.15-4.25 (1H, m), 4.85-4.9 (1H, m). MS *m/z*: 203 (M<sup>+</sup>-I, <sup>130</sup>Te), 201 (M<sup>+</sup>-I, <sup>128</sup>Te), 199 (M<sup>+</sup>-I, <sup>126</sup>Te), 146, 143, 141, 139, 130, 128, 126, 105, 77, 59. HRMS: Calcd for C<sub>4</sub>H<sub>9</sub>OTe (M<sup>+</sup>-I): 202.9722 (<sup>130</sup>Te), 200.9708 (<sup>128</sup>Te). Found: 202.9727 (<sup>130</sup>Te), 200.9714 (<sup>128</sup>Te).

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