# HALOGEN EXCHANGE REACTION OF OPTICALLY PURE HALOTELLURANES

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**Abstract** – A series of optically pure chlorotelluranes (**2a-c**) has been prepared by using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. Fluoro, bromo, and iodotelluranes (**1**,**3**, and **4**) were also prepared by the halogen exchange reaction of **2** in the presence of NaX, AgX, or tetrabutylammonium halide (TBAX) (X = halogen). The retention of the stereochemistry of chiral tellurium atom was observed throughout the reaction. An $S_N1$ pathway was proposed as the mechanism of this halogen exchange reaction.

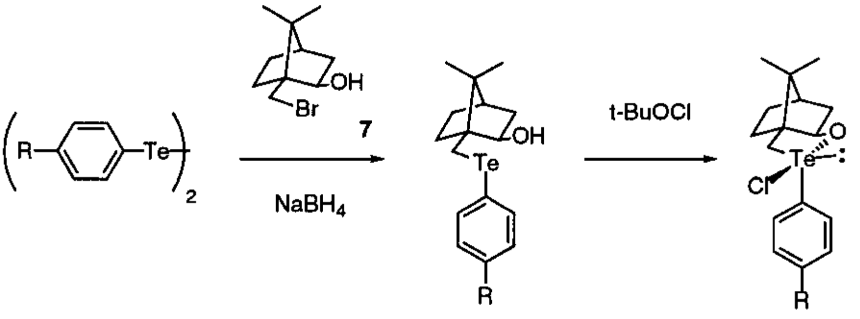
Organochalcogen compounds have unique chemical properties which provided many novel reactions in organic synthesis. Organosulfur[1] and organoselenium[2] compounds have been extensively studied, and they are now frequently used in organic synthesis. Compared to organosulfur and organoselenium compounds, organotellurium compounds have attracted less attention. Especially, little is known about the stereochemistry of optically active organotellurium compounds.[3]

During our studies of optically active organosulfur and organoselenium compounds, we found that 2-*exo*-hydroxy-10-bornyl group is a suitable chiral ligand for the preparation of optically pure organosulfur[4] and organoselenium[5,6] compounds which have a chiral center on the sulfur or selenium atom. Very recently, we reported the first synthesis of optically pure halotelluranes.[7] In this paper we report the details of the halogen exchange reactions of optically pure halotellulanes.

Standard procedure for the preparation of the corresponding haloselenuranes[5] was applied for the first synthesis of optically active halotelluranes (**2a-c**) (Scheme 1). Thus, (1S)-10-bromo-2-*exo*-borneol[8] reacted with sodium aryltellulate which was generated *in situ* to give the tellurides (**6a-c**). The tellurides (**6a-c**) were oxidized with *t*-BuOCl to give the corresponding chlorotelluranes (**2a-c**) as single diastereomers in excellent yields.

In order to understand the chemical properties of the halotelluranes, we studied the halogen exchange reaction of **1-4**, which were prepared from **2** (*vide infra*). The halotelluranes (**1-4**) were treated with a suspension of AgX or NaX (X=halogen), or a solution of tetrabutylammonium salt (TBAX, X=halogen) in dry MeCN (eq. 1). The results are summarized in Tables 1-3.

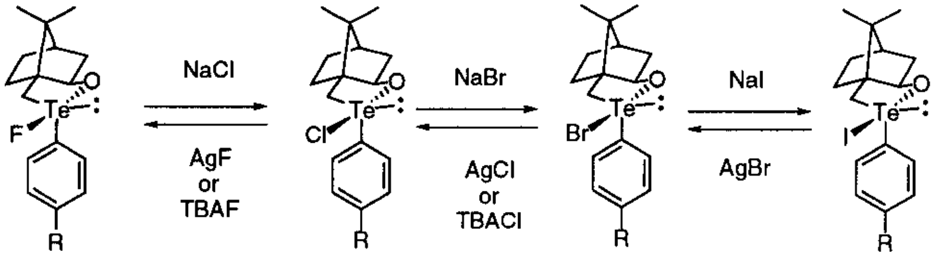
**Scheme 1**



**5a** (R = H)
**5b** (R = OMe)
**5c** (R = CF$_3$)

**6a** (R = H)
**6b** (R = OMe)
**6c** (R = CF$_3$)

**2a** (R = H)
**2b** (R = OMe)
**2c** (R = CF$_3$)



(1)

**1a** (R = H)
**1b** (R = OMe)
**1c** (R = CF$_3$)

**2a** (R = H)
**2b** (R = OMe)
**2c** (R = CF$_3$)

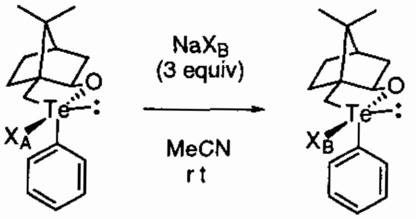
**3a** (R = H)
**3b** (R = OMe)
**3c** (R = CF$_3$)

**4a** (R = H)

It was necessary to use the corresponding sodium salt to convert a small halogen atom attached to the halotellurane into a larger halogen atom. On the other hand, a large halogen atom attached to the halotellurane was converted to a smaller halogen atom in the presence of the corresponding silver salt or tetrabutylammonium salt. Only a trace amount of a halotellurane was converted to the other halotellurane when a halotellurane with a large halogen atom reacted with a sodium salt of a small halogen atom, or a halotellurane with a small halogen atom reacted with a silver salt of a large halogen atom.

The result of the reaction of **1a**-**3a** with homogeneous solution of tetrabutylammonium salt gave us further information concerning the mechanism of this reaction (Table 3). A solution of halotellurane (**1a**-**3a**) reacted with TBAX to give a mixture of halotelluranes. The ratio of chlorotellurane to bromotellurane was identical when 1 equiv of TBACl was added to a solution of bromotellurane (**3a**) or 1 equiv of TBABr was added to a solution of chlorotellurane (**2a**) (Table 3, entries 4, 6). In the presence of 3 equiv of TBABr instead of 1 equiv of TBABr, the ratio of chlorotellurane (**2a**) to bromotellurane (**3a**) decreased (Table 3, entry 5). These results suggest that there is an equilibrium between the four species in this homogeneous system (eq. 2). The rate of the interconversion should be very fast since NMR study of the reaction of **2a** with TBAF showed that the halogen exchange reaction is instantaneous at room temperature.

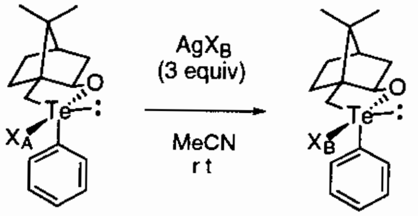
**Table 1.** Halogen Exchange Reaction of **1a**-**4a** in the Presence of NaX



| entry | $X_A$ | $X_B$ | time (h) | recovery[a] (%, $X=X_A$) | yield[a] (%, $X=X_B$) |
|---|---|---|---|---|---|
| 1 | F | Cl | 15 | 0 | 76 |
| 2 | Cl | F | 120 | 80 | trace |
| 3 | Cl | Br | 3 | 0 | 80 |
| 4 | Br | Cl | 120 | 78 | 0 |
| 5 | Br | I | 2 | 0 | 85 |
| 6 | I | Br | 120 | 84 | 0 |

a. Isolated yields.

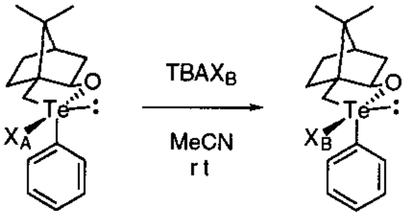
**Table 2.** Halogen Exchange Reaction of **1a**-**4a** in the Presence of AgX



| entry | $X_A$ | $X_B$ | time (h) | recovery[a] (%, $X=X_A$) | yield[a] (%, $X=X_B$) |
|---|---|---|---|---|---|
| 1 | F | Cl | 120 | 87 | trace |
| 2 | Cl | F | 3 | 0 | 86 |
| 3 | Cl | Br | 120 | 80 | 0 |
| 4 | Br | Cl | 16 | 0 | 83 |
| 5 | Br | I | 120 | 86 | 0 |
| 6 | I | Br | 10 | 0 | 79 |

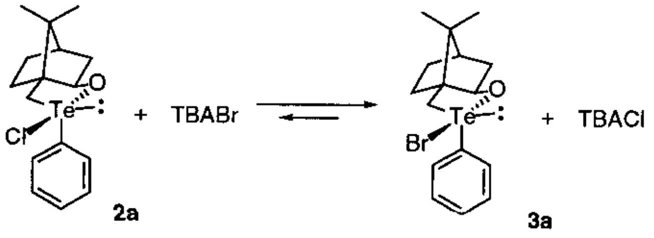
a. Isolated yields.

**Table 3.** Halogen Exchange Reaction of **1a**-**3a** in the Presence of TBAX



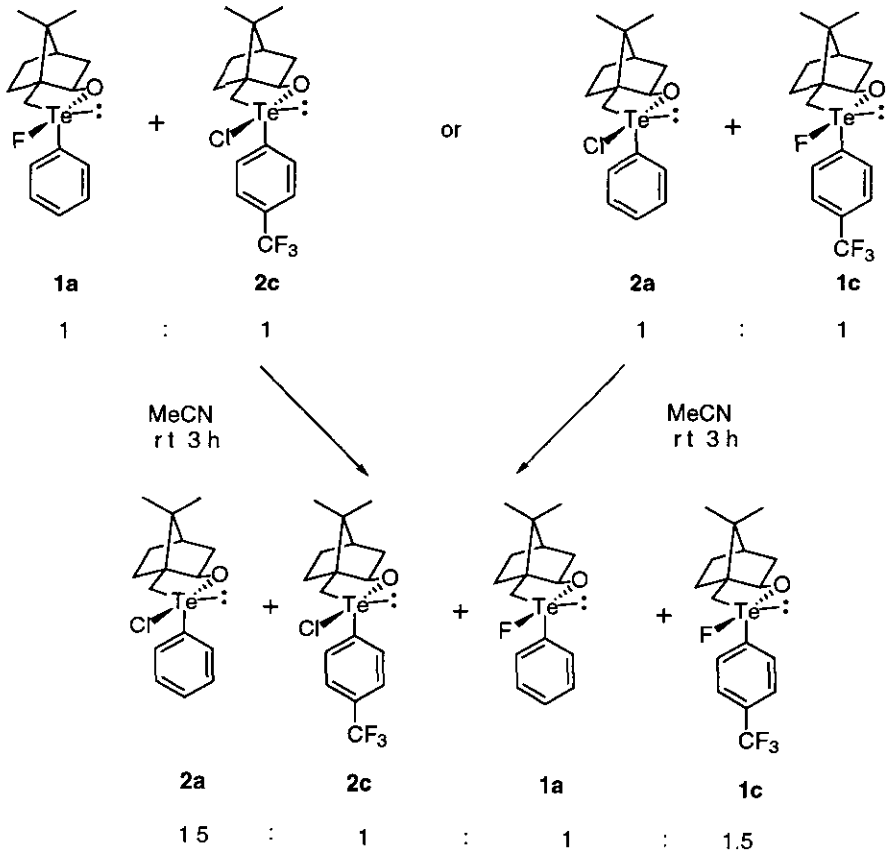
| entry | $X_A$ | $X_B$ | time (h) | $TBAX_B$ (equiv) | ratio[a] $[X=X_A] : [X=X_B]$ |
|---|---|---|---|---|---|
| 1 | F | Cl | 3 | 1 | 95 : 5> |
| 2 | F | Cl | 3 | 3 | 95 : 5> |
| 3 | Cl | F | 3 | 1 | 5> : 95 |
| 4 | Cl | Br | 3 | 1 | 84 : 16 |
| 5 | Cl | Br | 3 | 3 | 75 : 25 |
| 6 | Br | Cl | 3 | 1 | 16 : 84 |

a. The ratio was determined by the NMR integration.

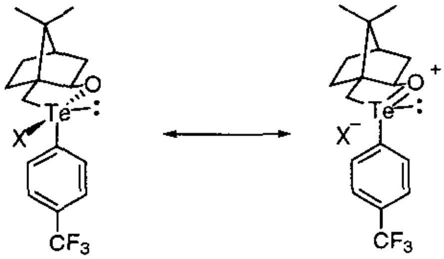


(2)

We also found that the halogen exchange reaction took place between the halotelluranes. Thus, **1a** and **2c**, or **2a** and **1c** reacted in MeCN to give a mixture of four products (**1a**, **1c**, **2a**, and **2c**) as shown in eq. 3. The observed ratio of the products (**2a** : **2c** : **1a** : **1c** = 1.5 : 1 : 1 : 1.5) indicated that the affinity of the tellurium atom for the halogen atom was slightly affected by the substituents on the phenyl ring. It is noteworthy that the affinity of the tellurium atom for the chlorine atom is reduced in the presence of a electron-withdrawing group on the phenyl ring. It may be possible to explain this result in terms of the back donation of a lone pair of the oxygen atom as shown in eq. 4. The presence of an electron-withdrawing group in the phenyl ring may cause a stronger back donation of the oxygen lone pair, and the formation of more ionic Te-F bond may be favored under the situation.

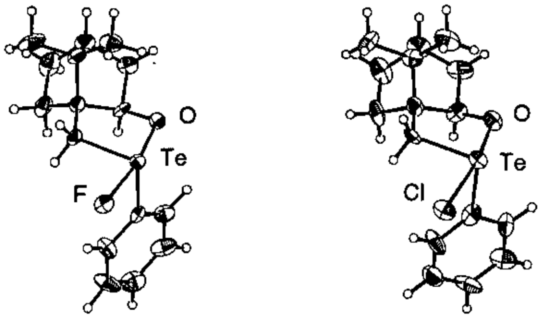


(3)



(4)

The absolute stereochemistry of halotelluranes was confirmed to be R by X-ray crystallographic analysis, as expected from the results we reported in a selenium analog.[5-7] The retention of the stereochemistry throughout the interconversion between the halotelluranes is indicated by the spectral similarity among **1-4**, and it is confirmed by comparing the X-ray crystal structure of **1a**[7] and **2a**[9] (Figure 1).



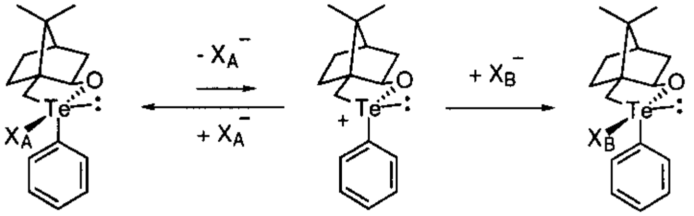
**1a** **2a**

**Figure 1.** Perspective structure of **1a**[7] and **2a**.

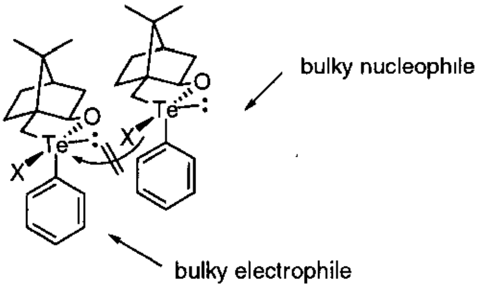
It is noteworthy that both **1a** and **2a** have distorted trigonal bipyramidal structures, and the only significant difference is the distance between the halogen atom and tellurium atom: the bond distance of Te-F was 2.063(7) Å, while the distance of Te-Cl range from 2.59(1) - 2.663(10) Å.[10]

We propose the mechanism of the halogen exchange reaction as shown in Scheme 2.

**Scheme 2**



It is less likely that halogen is exchanged *via* $S_N2$ or an associative pathway since the retention of the stereochemistry was observed. The exchange of the counter anion could be explained in terms of the formation of alkoxytelluronium ion, followed by the recombination with another counter anion. The halogen exchange reaction between the halotelluranes should be explained similarly. Though it may be possible to explain the mechanism of this reaction in terms of an $S_N2$-like reaction followed by the rapid isomerization of the halotellurane, it is very difficult to explain the halogen exchange reaction between the halotelluranes since halotellurane is a bulky nucleophile (and at the same time it is a bulky electrophile) (eq.5).



(5)

From the results of the halogen exchange reaction of halotelluranes with AgX or NaX (X=halogen) (Tables 1, 2), we concluded that the hardness[11] of alkoxytelluronium ions lies between hard $Na^+$ and soft $Ag^+$.

In summary, we have shown that the halogen exchange reaction of halotelluranes took place in the presence of AgX, NaX or TBAX (X=halogen). We have also shown that the halogen exchange reaction between the halotelluranes easily took place. The mechanism of this reaction could be explained in terms of the dissociation of the halotellurane into alkoxytelluronium ion and counter anion.

## ACKNOWLEDGEMENT

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## EXPERIMENTAL

Melting points were determined on a Yanako micromelting point apparatus and are uncorrected. Spectroscopic measurements were carried out with the following instruments: optical rotations, JASCO DIP-1000 digital polarimeter; IR spectra, Perkin-Elmer 1600 Series FTIR; mass (MS) and high resolution mass spectra (HRMS), JEOL JMS-D 200 and JMS-AX 505H; $^1$H-NMR spectra Varian Gemini-300 (300 MHz) for solutions in $CDCl_3$ with $Me_4Si$ as an internal standard; $^{13}$C-NMR spectra Varian Gemini-300 (75 MHz) for solutions in $CDCl_3$ with $^{13}CDCl_3$ (77 ppm) as an internal standard. Dichloromethane was distilled from $P_2O_5$ and stored over 4A molecular sieves. Column chromatography was performed on Kiesel gel 60 (Merck, 230-400 mesh). Bis[(4-trifluoromethyl)phenyl]ditelluride and bis(4-methoxyphenyl)ditelluride were prepared according to literature procedures.[12]

**(1S)-10-(Phenyltellurenyl)-2-*exo*-borneol (6a)**: To a solution of (1S)-10-bromo-2-*exo*-borneol[8] (466 mg, 2.0 mmol) in EtOH (20 mL) were added diphenylditelluride (450 mg, 1.1 mmol) and $NaBH_4$ (114 mg, 3.0 mmol) at rt. After reflux under an Ar atmosphere for 2 h, $NaBH_4$ (50 mg, 1.3 mmol) was added and the whole reaction mixture was refluxed for 1 h. After evaporation of the solvent, $CH_2Cl_2$ (20 mL) and saturated $NH_4Cl$ were added to the mixture. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (10 mL x 2). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was subjected to column chromatography (hexane/AcOEt 10:1) to give 561 mg (78%) of telluride (**6a**): orange oil; $[\alpha]_D^{26}$ +15.0 ° (*c* 1.55, $CHCl_3$); IR (neat) 3854, 3456, 1574, 1474, 1070, 1018, 731, 691 $cm^{-1}$; $^1$H NMR δ: 0.85 (s, 3H), 0.80-1.20 (m, 2H), 1.04 (s, 3H), 1.40-1.90 (m, 6H), 3.05 and 3.11 (ABq, *J* = 11.0 Hz, 2H), 3.81 (ddd, J = 3.8, 3.8, 7.7 Hz, 1H), 7.18-7.32 (m, 3H), 7.77-7.81 (m, 2H); $^{13}$C NMR δ: 10.6 ($CH_2$), 20.2 ($CH_3$), 20.8 ($CH_3$), 27.1 ($CH_2$), 33.7 ($CH_2$), 39.6 ($CH_2$), 45.9 (CH), 47.8 (C), 53.3 (C), 78.6 (CH), 111.6 (C), 128.0(CH), 129.5 (CH x 2), 138.8 (CH x 2); MS *m/z*: 360 ($M^+$) ($^{130}$Te), 358 ($M^+$) ($^{128}$Te), 356 ($M^+$) ($^{126}$Te); HRMS Calcd for $C_{16}H_{22}O^{130}Te$: 360.0739. Found: 360.0738, Calcd for $C_{16}H_{22}O^{126}Te$: 356.0710. Found: 356.0710.

**(1S)-10-(4-Methoxyphenyltellurenyl)-2-*exo*-borneol (6b)**: The procedure described in the preparation of **6a** was generally followed to prepare **6b** from (1S)-10-bromo-2-*exo*-borneol (**7**)[8] and ditelluride (**5b**). **6b**: yield 51%, orange oil; $[\alpha]_D^{27}$ +26.5 ° (*c* 1.32, $CHCl_3$); IR (neat) 3564, 2949, 2362, 1654, 1586, 1488, 1244, 821 $cm^{-1}$; $^1H$ NMR δ: 0.82 (s, 3H), 0.90-1.86 (m, 8H), 1.01 (s, 3H), 2.94 and 3.04 (ABq, *J* = 11.3 Hz, 2H), 3.76-3.83 (m, 1H), 3.79 (s, 3H), 6.74-6.79 (m, 2H), 7.72-7.77 (m, 2H); $^{13}C$ NMR δ: 10.9 ($CH_2$), 20.1 ($CH_3$), 20.8 ($CH_3$), 27.1 ($CH_2$), 33.7 ($CH_2$), 39.5 ($CH_2$), 45.9 (CH), 47.7 (C), 53.3 (C), 55.3 ($CH_3$), 78.5 (CH), 100.2 (C), 115.6 (CH x 2), 141.3 (CH x 2), 160.0 (C); MS *m/z*: 390 ($M^+$) ($^{130}Te$), 388 ($M^+$) ($^{128}Te$), 386 ($M^+$) ($^{126}Te$); HRMS Calcd for $C_{17}H_{24}O_2{}^{130}Te$: 390.0845. Found: 390.0833, Calcd for $C_{17}H_{24}O_2{}^{128}Te$: 388.0832. Found: 388.0819.

**(1S)-10-[4-(Trifluoromethyl)phenyltellurenyl]-2-*exo*-borneol (6c)**: The procedure described in the preparation of **6a** was generally followed to prepare **6c** from (1S)-10-bromo-2-*exo*-borneol (7)[8] and ditelluride (**5c**). **6c**: yield 51%, orange oil; $[\alpha]_D^{25}$ -17.4 ° (*c* 2.75, $CHCl_3$); IR (neat) 3482, 2952, 1598, 1393, 1325, 1166, 1126, 1073, 1011, 680 $cm^{-1}$; $^1H$ NMR δ: 0.87 (s, 3H), 0.82-1.98 (m, 8H), 1.07 (s, 3H), 3.10 and 3.18 (ABq, *J* = 11.3 Hz, 2H), 3.82 (ddd, *J* = 3.8, 3.8, 7.7 Hz, 1H), 7.41-7.44 (m, 2H), 7.82-7.85 (m, 2H); $^{13}C$ NMR δ: 10.9 ($CH_2$), 20.2 ($CH_3$), 20.8 ($CH_3$), 27.1 ($CH_2$), 33.7 ($CH_2$), 40.0 (C) 40.1 ($CH_2$), 45.9 (CH), 48.0 (C), 53.2 (C), 78.6 (CH), 125.9 (CH x 2), 126.1 (C) 137.9 (CH x 2), 138.0 (C); MS *m/z*: 428 ($M^+$) ($^{130}Te$), 426 ($M^+$) ($^{128}Te$), 424 ($M^+$) ($^{126}Te$); HRMS Calcd for $C_{17}H_{21}OF_3{}^{130}Te$: 428.0614. Found: 428.0612.

**(1S,$R_{Te}$)-5-Chloro-10,10-dimethyl-5-phenyl-5λ$^4$-tellura-4-oxatricyclo[5.2.1.0$^{3,7}$]-decane (2a)**. To a solution of **6a** (500 mg, 1.40 mmol) in dry $CH_2Cl_2$ (20 mL) was added *t*-BuOCl (158 µA, 1.40 mmol) under an Ar atmosphere at 0 °C.The whole mixture was stirred at 0 °C for 20 min and the solvent was evaporated. The residue was recrystallized from hexane/AcOEt to give 526 mg (96 %) of chlorotellurane (**2a**), mp 154-156 °C (colorless prisms); $[\alpha]_D^{26}$ +92.3 ° (*c* 0.993, $CHCl_3$); IR (KBr) 3048, 2984, 2947, 2871, 1481, 1453, 1436, 1017, 990, 734, 687 $cm^{-1}$; $^1H$ NMR δ: 0.91 (s, 3H), 0.85-1.20 (m, 2H), 1.14 (s, 3H), 1.60-2.00 (m, 5H), 3.42 and 3.62 (ABq, *J* = 13.4 Hz, 2H), 3.81 (dd, J = 3.3 Hz, 1H), 7.50-7.60 (m, 3H), 8.10-8.20 (m, 2H); $^{13}C$ NMR δ: 20.5 ($CH_3$), 20.7 ($CH_3$), 26.8 ($CH_2$), 31.4 ($CH_2$), 41.9 ($CH_2$), 44.0 (CH), 45.6 ($CH_2$), 46.7 (C), 55.4(C), 93.2 (CH), 130.2 (CH x 2), 130.9 (C), 131.4 (CH), 132.1 (CH x 2); MS *m/z*: 395 ($M^+$ - 1) ($^{130}Te$, $^{37}Cl$), 394 ($M^+$) ($^{130}Te$, $^{35}Cl$), 393 ($M^+$ - 1) ($^{130}Te$, $^{35}Cl/^{128}Te$, $^{37}Cl$), 392 ($M^+$) ($^{128}Te$, $^{35}Cl/^{126}Te$, $^{37}Cl$), 391 ($M^+$ - 1) ($^{128}Te$, $^{35}Cl/^{126}Te$, $^{37}Cl$), 390 ($M^+$) ($^{126}Te$, $^{35}Cl$), 389 ($M^+$ - 1) ($^{126}Te$, $^{35}Cl$); Anal. Calcd for $C_{16}H_{21}OClTe$: C, 48.97; H, 5.39. Found: C, 48.97; H, 5.36.

**(1S,$R_{Te}$)-5-Chloro-10,10-dimethyl-5-(4-methoxyphenyl)-5λ$^4$-tellura-4-oxatricyclo-[5.2.1.0$^{3,7}$]decane (2b)**: The procedure described in the preparation of **2a** was generally followed to prepare **2b** from **6b**. **2b**: yield 84%, mp 115-118 °C (colorless prisms, recrystallized from hexane/AcOEt); $[\alpha]_D^{27}$ +93.3 ° (*c* 1.03, $CHCl_3$); IR (KBr) 2951, 1493, 1296, 1256, 1179, 1020, 591 $cm^{-1}$; $^1H$ NMR δ: 0.90 (s, 3H), 0.88-1.26 (m, 2H), 1.13 (s, 3H), 1.54-1.92 (m, 5H), 3.37 and 3.60 (ABq, *J* = 13.2 Hz, 2H), 3.83-3.87 (m, 1H), 3.87 (s, 3H), 7.05 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H); $^{13}C$ NMR δ: 20.3 ($CH_3$), 20.5 ($CH_3$), 26.6 ($CH_2$), 31.2 ($CH_2$), 41.7 ($CH_2$), 43.9 (CH), 45.4 ($CH_2$), 46.5 (C), 55.3 (C), 55.4 ($CH_3$), 93.0 (CH), 115.5 (CH x 2), 120.3 (C), 133.4 (CH x 2), 161.9 (C); MS *m/z*: 426 ($M^+$)

($^{130}$Te, $^{37}$Cl), 424 (M$^{+}$) ($^{130}$Te, $^{35}$Cl/$^{128}$Te, $^{37}$Cl), 422 (M$^{+}$) ($^{128}$Te, $^{35}$Cl/$^{126}$Te, $^{37}$Cl), 420 (M$^{+}$) ($^{126}$Te, $^{35}$Cl); Anal. Calcd for $C_{17}H_{23}O_2ClTe$: C, 48.34; H, 5.49. Found: C, 48.32; H, 5.30.

**(1S,R$_{Te}$)-5-Chloro-10,10-dimethyl-5-[4-(trifluoromethyl)phenyl]-5λ$^{4}$-tellura-4-oxatricyclo[5.2.1.0$^{3,7}$]decane (2c)**: The procedure described in the preparation of **2a** was generally followed to prepare **2c** from **6c**. **2c**: yield 82%, mp 165-167 °C (colorless prisms, recrystallized from hexane/AcOEt); $[\alpha]_D^{27}$ +102.3 ° (*c* 1.05, $CHCl_3$); IR (KBr) 2955, 2878, 1456, 1396, 1330, 1167, 1129, 1074, 829, 597 cm$^{-1}$; $^{1}$H NMR δ: 0.92 (s, 3H), 0.82-1.30 (m, 2H), 1.14 (s, 3H), 1.17-1.94 (m, 5H), 3.44 and 3.65 (ABq, *J* = 13.2 Hz, 2H), 3.79 (dd, *J* = 2.7, 7.1, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 8.32 (d, *J* = 8.2 Hz, 2H); $^{13}$C NMR δ: 20.4 ($CH_3$), 20.8 ($CH_3$), 26.8 ($CH_2$), 31.4 ($CH_2$), 41.8 ($CH_2$), 44.5 (CH), 45.5 ($CH_2$), 46.8 (C), 55.4 (C), 93.3 (CH), 126.7 (C), 126.8 (CH x 2), 126.9 (C), 132.8 (CH x 2), 135.1 (C); MS *m/z*: 462 (M$^{+}$) ($^{130}$Te, $^{35}$Cl/$^{128}$Te, $^{37}$Cl); Anal. Calcd for $C_{17}H_{20}OClF_3Te$: C, 44.35; H, 4.38. Found: C, 44.15; H, 4.30.

### General Procedure for the Halogen Exchange Reaction of Halotelluranes in the Presence of NaX or AgX (X=halogen).

To a solution of a halotellurane (0.10 mmol) in dry MeCN (3 mL) was added NaX or AgX (0.30 mmol) under a $N_2$ atmosphere. The whole mixture was stirred at rt for the specified period and the precipitates were filtered off with $CH_2Cl_2$. The filtrate was evaporated to give the product.

**(1S,R$_{Te}$)-10,10-Dimethyl-5-fluoro-5-phenyl-5λ$^{4}$-tellura-4-oxatricyclo[5.2.1.0$^{3,7}$]decane (1a)** The general procedure was followed to prepare **1a** from **2a** and AgF. The whole mixture was stirred for 3 h. **1a**: yield 86%, mp 137-140 °C (colorless prisms, recrystallized from hexane-AcOEt); $[\alpha]_D^{25}$ -26.5 ° (*c* 1.02, $CHCl_3$); IR (KBr) 3056, 2952, 2871, 1576, 1438, 1049, 1020, 872, 741, 688 cm$^{-1}$; $^{1}$H NMR δ: 0.91 (s, 3H), 0.85-1.20 (m, 2H), 1.10 (s, 3H), 1.60-2.00 (m, 5H), 2.89 and 3.21 (ABq, *J* = 13.2 Hz, 2H), 3.74 (dd, J = 3.3, 7.1 Hz, 1H), 7.40-7.60 (m, 3H), 7.92-7.96 (m, 2H); $^{13}$C NMR δ: 20.6 ($CH_3$), 20.8 ($CH_3$), 27.1 ($CH_2$), 31.5 ($CH_2$), 37.0 (CH), 41.5 ($CH_2$), 45.5 ($CH_2$), 46.6 (C), 55.1 (C), 90.0 (CH), 130.1 (CH x 2), 131.2 (CH), 131.8 (CH x 2), 132.9 (C); MS *m/z*: 378 (M$^{+}$) ($^{130}$Te), 376 (M$^{+}$) ($^{128}$Te), 374 (M$^{+}$) ($^{126}$Te); Anal. Calcd for $C_{16}H_{21}OFTe$: C, 51.12; H, 5.63. Found: C, 50.86; H, 5.75.

**(1S,R$_{Te}$)-10,10-Dimethyl-5-fluoro-5-(4-methoxyphenyl)-5λ$^{4}$-tellura-4-oxatricyclo-[5.2.1.0$^{3,7}$]decane (1b)** The general procedure was followed to prepare **1b** from **2b** and AgF. The whole mixture was stirred for 1 h. **1b**: yield 88%, colorless oil; $[\alpha]_D^{25}$ -33.4 ° (*c* 1.05, $CHCl_3$); IR (neat) 2951, 1588, 1491, 1252, 1177, 754 cm$^{-1}$; $^{1}$H NMR δ: 0.90 (s, 3H), 0.92-1.14 (m, 2H), 1.09 (s, 3H), 1.64-1.88 (m, 5H), 2.81 and 3.17 (ABq, *J* = 13.2 Hz, 2H), 3.75 (dd, J = 3.6, 6.7 Hz, 1H), 3.86 (s, 3H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H); $^{13}$C NMR δ: 20.6 ($CH_3$), 20.7 ($CH_3$), 27.1 ($CH_2$), 31.5 ($CH_2$), 37.1 (CH), 41.5 ($CH_2$), 45.4 ($CH_2$), 46.5 (C), 55.0 (C), 55.5 ($CH_3$), 89.7 (CH), 115.6 (CH x 2), 122.5 (C), 133.1 (CH x 2), 162.0 (C); MS *m/z*: 408 (M$^{+}$) ($^{130}$Te), 406 (M$^{+}$) ($^{128}$Te), 404 (M$^{+}$) ($^{126}$Te); HRMS Calcd for $C_{17}H_{23}O_2F^{130}Te$: 390.0845. Found: 390.0833. Calcd for $C_{17}H_{24}O_2{}^{128}Te$: 388.0832. Found: 388.0819.

**(1S,R$_{Te}$)-10,10-Dimethyl-5-fluoro-5-[(4-trifluoromethyl)phenyl]-5λ$^{4}$-tellura-4-oxatricyclo[5.2.1.0$^{3,7}$]decane (1c)** The general procedure was followed to prepare **1c** from **2c** and AgF. The whole mixture was stirred for 1 h. **1c**: yield 90%, mp 90-92 °C (colorless prisms, recrystallized from hexane-AcOEt); $[\alpha]_D^{27}$ -21.3 ° (*c* 1.01, $CHCl_3$); IR (KBr) 2955, 1602, 1396, 1325, 1168, 1131, 1072 cm$^{-1}$; $^{1}H$ NMR δ: 0.91 (s, 3H), 0.82-1.30 (m, 2H), 1.10 (s, 3H), 1.63-1.93 (m, 5H), 2.89 and 3.22 (ABq, *J* = 13.2 Hz, 2H), 3.72 (dd, *J* = 3.6, 6.9, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 8.12 (d, *J* = 7.7 Hz, 2H); $^{13}C$ NMR δ: 20.6 ($CH_3$), 20.8 ($CH_3$), 27.0 ($CH_2$), 31.4 ($CH_2$), 37.1 (CH), 41.4 ($CH_2$), 45.3 ($CH_2$), 46.6 (C), 55.0 (C), 90.0 (CH), 126.6 (C), 126.7 (CH x 2), 132.5 (C), 132.5 (CH x 2), 133.5 (C); MS *m/z*: 446 ($M^+$) ($^{130}Te$), 444 ($M^+$) ($^{128}Te$), 442 ($M^+$) ($^{126}Te$); Anal. Calcd for $C_{17}H_{20}OF_4Te$: C, 45.99; H, 4.54. Found: C, 46.27; H, 4.56.

**(1S,R$_{Te}$)-5-Bromo-10,10-dimethyl-5-phenyl-5λ$^{4}$-tellura-4-oxatricyclo[5.2.1.0$^{3,7}$]decane (3a)** The general procedure was followed to prepare **3a** from **2a** and NaBr. The whole mixture was stirred for 3 h. **3a**: yield 80%, mp 143-144 °C (colorless prisms, recrystallized from hexane-AcOEt); $[\alpha]_D^{25}$ +143.5 ° (*c* 1.00, $CHCl_3$); IR (KBr) 3047, 2939, 2868, 1435, 1045, 733 cm$^{-1}$; $^{1}H$ NMR δ: 0.89 (s, 3H), 0.80-1.20 (m, 2H), 1.13 (s, 3H), 1.60-1.95 (m, 5H), 3.58 and 3.74 (ABq, *J* = 13.2 Hz, 2H), 3.80-3.85 (m, 1H), 7.50-7.60 (m, 3H), 8.10-8.20 (m, 2H); $^{13}C$ NMR δ: 20.4 ($CH_3$), 20.6 ($CH_3$), 26.7 ($CH_2$), 31.4 ($CH_2$), 42.1 ($CH_2$), 44.9 (CH), 45.5 ($CH_2$), 46.7 (C), 55.5 (C), 93.8 (CH), 129.4 (C), 130.2 (CH x 2), 131.4 (CH), 132.5 (CH x 2); MS *m/z*: 441 ($M^+$ + 1) ($^{130}Te$, $^{81}Br$), 440 ($M^+$) ($^{130}Te$, $^{81}Br$), 439 ($M^+$ + 1) ($^{130}Te$, $^{79}Br$/$^{128}Te$, $^{81}Br$)/($M^+$ - 1) ($^{130}Te$, $^{81}Br$), 438 ($M^+$) ($^{130}Te$, $^{79}Br$/$^{128}Te$, $^{81}Br$), 437 ($M^+$ + 1) ($^{128}Te$, $^{79}Br$/$^{126}Te$, $^{81}Br$)/($M^+$ - 1) ($^{130}Te$, $^{79}Br$/$^{130}Te$, $^{81}Br$), 436 ($M^+$) ($^{128}Te$, $^{79}Br$/$^{126}Te$, $^{81}Br$), 435 ($M^+$ + 1) ($^{126}Te$, $^{79}Br$)/($M^+$ - 1) ($^{128}Te$, $^{79}Br$/$^{126}Te$, $^{81}Br$), 434 ($M^+$) ($^{126}Te$, $^{79}Br$), 433 ($M^+$ - 1) ($^{126}Te$, $^{79}Br$); Anal. Calcd for $C_{16}H_{21}OBrTe$: C, 43.99; H, 4.85. Found: C, 44.04; H, 4.79.

**(1S,R$_{Te}$)-5-Bromo-10,10-dimethyl-5-(4-methoxylphenyl)-5λ$^{4}$-tellura-4-oxatricyclo-[5.2.1.0$^{3,7}$]decane (3b)** The general procedure was followed to prepare **3b** from **2b** and NaBr. The whole mixture was stirred for 12 h. **3b**: yield 81%, mp 135-137 °C (colorless prisms, recrystallized from hexane-AcOEt); $[\alpha]_D^{26}$ +131.6 ° (*c* 1.32, $CHCl_3$); IR (KBr) 2942, 2875, 1586, 1493, 1256, 1181, 1046, 1018, 822, 586 cm$^{-1}$; $^{1}H$ NMR δ: 0.90 (s, 3H), 0.86-1.29 (m, 2H), 1.14 (s, 3H), 1.55-1.90 (m, 5H), 3.54 and 3.74 (ABq, *J* = 13.2 Hz, 2H), 3.87 (dd, *J* = 1.6, 7.1 Hz, 1H), 3.87 (s, 3H), 7.04 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 9.3 Hz, 2H); $^{13}C$ NMR δ: 20.3 ($CH_3$), 20.5 ($CH_3$), 26.6 ($CH_2$), 31.2 ($CH_2$), 41.9 ($CH_2$), 45.0 (CH), 45.4 ($CH_2$), 46.6 (C), 55.4 (C), 55.5 ($CH_3$), 93.7 (CH), 115.6 (CH x 2), 133.9 (CH x 2), 161.9 (C); MS *m/z*: 470 ($M^+$) ($^{130}Te$, $^{81}Br$), 468 ($M^+$) ($^{130}Te$, $^{79}Br$/$^{128}Te$, $^{81}Br$); Anal. Calcd for $C_{17}H_{23}O_2BrTe$: C, 43.74; H, 4.97. Found: C, 43.54; H, 4.90

**(1S,R$_{Te}$)-5-Bromo-10,10-dimethyl-5-[4-(trifluoromethyl)phenyl]-5λ$^{4}$-tellura-4-oxatricyclo[5.2.1.0$^{3,7}$]decane (3c)** The general procedure was followed to prepare **3c** from **2c** and NaBr. The whole mixture was stirred for 3 h. **3c**: yield 76%, mp 152-154 °C (colorless prisms, recrystallized from hexane-AcOEt); $[\alpha]_D^{27}$ +117.3 ° (*c* 1.01, $CHCl_3$); IR (KBr) 2953, 1395, 1326, 1168, 1129, 1073, 1047, 594 cm$^{-1}$; $^{1}H$ NMR δ: 0.92 (s, 3H), 0.88-1.25 (m, 2H), 1.15 (s, 3H), 1.63-1.92 (m, 5H), 3.61 and 3.78 (ABq, $J$ = 13.2 Hz, 2H), 3.80-3.83 (m, 1H), 7.78 (d, $J$ = 8.2 Hz, 2H), 8.35 (d, $J$ = 8.2 Hz, 2H); $^{13}$C NMR δ: 20.2 ($CH_3$), 20.5 ($CH_3$), 26.5 ($CH_2$), 31.1 ($CH_2$), 41.9 ($CH_2$), 45.3 (CH), 45.3 ($CH_2$), 46.6 (C), 55.3 (C), 93.8 (CH), 126.7 (C), 133.1 (CH x 2), 133.2 (C), 133.2 (CH x 2), 133.4 (C); MS $m/z$: 508 ($M^+$) ($^{130}$Te, $^{81}$Br), 506 ($M^+$) ($^{130}$Te, $^{79}$Br/$^{128}$Te, $^{81}$Br), 504 ($M^+$) ($^{128}$Te, $^{79}$Br/$^{126}$Te, $^{81}$Br), 502 ($M^+$) ($^{126}$Te, $^{79}$Br); Anal. Calcd for $C_{17}H_{20}OBrF_3Te$: C, 40.45; H, 3.99. Found: C, 40.34; H, 3.84.

**(1S,R$_{Te}$)-5-Iodo-10,10-dimethyl-5-phenyl-5λ$^4$-tellura-4-oxatricyclo[5.2.1.0$^{3,7}$]-decane (4a)** The general procedure was followed to prepare **4a** from **3a** and NaI. The whole mixture was stirred for 2 h. **4a**: yield 85%, yellow oil; $[\alpha]_D^{27}$ +187.6 ° ($c$ 1.10, $CHCl_3$); IR ($CHCl_3$) 2946, 2857, 1440, 1368, 1342, 1074, 1043, 995, 866, 751, 687 cm$^{-1}$; $^1$H NMR δ: 0.91 (s, 3H), 0.90-1.30 (m, 2H), 1.15 (s, 3H), 1.60-1.95 (m, 5H), 3.82 and 3.92 (ABq, $J$ = 13.5 Hz, 2H), 3.86 (dd, $J$ = 3.3 Hz, 1H), 7.40-7.60 (m, 3H), 8.10-8.20 (m, 2H); $^{13}$C NMR δ: 20.5 ($CH_3$), 20.6 ($CH_3$), 26.7 ($CH_2$), 31.4 ($CH_2$), 42.5 ($CH_2$), 45.5 ($CH_2$), 45.8 (CH), 46.8 (C), 55.2 (C), 94.5 (CH), 127.0 (C), 130.2 (CH x 2), 131.3 (CH), 133.4 (CH x 2); MS $m/z$: 360 ($M^+$ - I + 1) ($^{130}$Te), 358 ($M^+$ - I + 1) ($^{128}$Te), 356 ($M^+$ - I + 1) ($^{126}$Te); HRMS Calcd for $C_{16}H_{21}O^{130}Te$ ($M^+$-I): 359.0661. Found: 359.0645, Calcd for $C_{16}H_{21}O^{128}Te$ ($M^+$-I): 357.0647. Found: 357.0618.

### General Procedure for the Halogen Exchange Reaction of Halotelluranes in the Presence of TBAX (X=halogen).

To a solution of TBAX (0.1 mmol) in dry MeCN (3 mL) was added **1a**, **2a**, or **3a** (0.1 mmol) under a $N_2$ atmosphere. The whole mixture was stirred at rt for 3 h and the solvent was removed by evaporation. The ratio of the halotelluranes was determined by the NMR integration of this crude sample (see, Table 3). The attempted purification by column chromatography or recrystallization was unsuccessful.

### Procedure for the Interconversion of Halotelluranes.

A solution of **1a** (10 mg, 0.027 mmol) and **2c** (12 mg, 0.027 mmol) in dry MeCN (0.8 mL) was stirred under a $N_2$ atmosphere at rt for 3 h. The solvent was removed by evaporation, and the ratio of the halotelluranes (see, eq. 3) was determined by the NMR integration of this crude sample. The reaction of **2a** with **1c** was carried out similarly.

### X-ray Diffraction Study of 2a.

A single crystal of **2a** was obtained by recrystallization of **2a** from hexane-$CH_2Cl_2$, and it was mounted on a glass fiber. The data was collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator, and the structure was solved by direct methods; all data reduction and structural refinements were performed with the teXsan crystal structure analysis package provided by Molecular Structure Corporation.

Crystallographic data for **2a**: trigonal, space group, $P3_1$ with a = 24.700(3) Å, c = 14.047(8) Å, V = 7425(4) Å$^3$, and Z = 18 ($d_{calcd}$ = 1.579 g cm$^{-3}$), μ (MoKα) = 19.56 cm$^{-1}$ absorption collected by ω scans; 10537 unique reflections; 4502 with $I > 3.00\sigma(I)$ were used in refinement; R = 6.7%, $R_w$ = 7.1%. All non-hydrogen atoms were refined with anisotropic parameters, and all hydrogen atoms included in the structural factor were placed in idealized positions. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge, CB2 1EZ(UK), on quoting the full journal citation.

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