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2-SUBSTITUTED ISOTELLUROCHROMENIUM SALT DERIVATIVES: PREPARATIONS, STRUCTURES, SPECTROSCOPIC PROPERTIES[1]

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Abstract – Several types of novel isotellurochromenium salt derivatives (**2-10**) were prepared from the isotellurochromenes (**1**). The isotellurochromenium tetrafluoroborates (**2**), triflates (**3-5**), tosylates (**6**) and mesylates (**7**) are telluronium salts, and the dihalogenoisotellurochromenes (**8-10**) are telluranes. The molecular structures of the isotellurochromenium tosylate (**6a**) and the dichloroisotellurochromene (**8a**) were characterized by an X-ray crystallographic analysis using the 3-*tert*-butyl derivatives.

INTRODUCTION

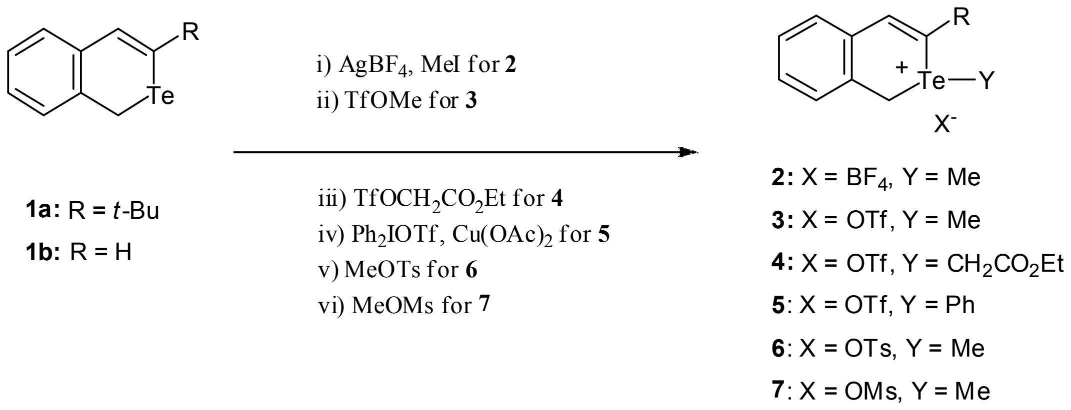
The chemistry of the telluronium salts has recently been developed in connection with that of hypervalent organotellurium compounds.[2] Generally, stable telluranes (tetravalent tellurium compounds),[3, 4] such as telluium tetrahalides, dialkyltelluride dihalides and tetraaryltelluranes, have a trigonal bipyramidal center on the tellurium cation and the tellurium-carbon bonds are composed three sp^2 and two p-orbitals, while the tellurium center of a telluronium salt[3, 4] has a tetrahedral and three equal sp^3 bonds. Various bivalent six-membered tellurium-containing mono-cyclic heterocycles, i.e., tetrahydropyrans, 2*H*-telluropyrans, 4*H*-telluropyrans, 4*H*-telluropyran-4-ones, and benzene-ring fused compounds, i.e., benzo tetrahydropyrans, 2*H*-tellurochromenes, 4*H*-tellurochromenes, 2*H*-tellurochromen-2-ones, 4*H*-tellurochromen-4-ones, and 1*H*-tellurochromen-1-ones have already been prepared,[5-7] and the structures of some have been unequivocally assigned based on single-crystal X-ray crystallographic analyses and NMR studies. Their basic and only limited reactivities, such as halogenation, alkylation and allylation, on the tellurium atom have been examined. Only NMR studies of the isoselenochromanes, relative six-membered selenium analogues have been reported by Hori and Kataoka *et al.*[8]

Previously, we succeeded in the synthesis of the novel isotellurochromenes (**1**), which are the six-membered tellurium heterocycles, and the transformation into the 2-benzotelluropyrylium salts,[9] six-membered aromatic heterocycles containing a tellurium cation. The 2-benzotelluropyrylium salts reacted with several nucleophiles,[10] such as alcohols, amines, the cyanide ion, a carbonyl compound (acetone), Grignard reagents, organocopper reagents[11] and allyltributyltin,[12] to give many 1-substituted isotellurochromenes. In addition, we reported that (*E*)-*o*-(2'-lithiovinyl)benzyllithium,[13] generated by the reaction of the isotellurochromenes **1** with BuLi, was useful as a 1,5-dilithiated synthetic building block. However, the simple reactivity has not yet been examined for the isotellurochromenes. In this paper, we report the preparation of the various types of isotellurochomenium salt derivatives by the alkylation, arylation and halogenation of the isotellurochromenes (**1**), and their spectroscopic properties including X-ray analyses.

RESULTS AND DISCUSSION

1. Preparation of isotellurochromenium salts

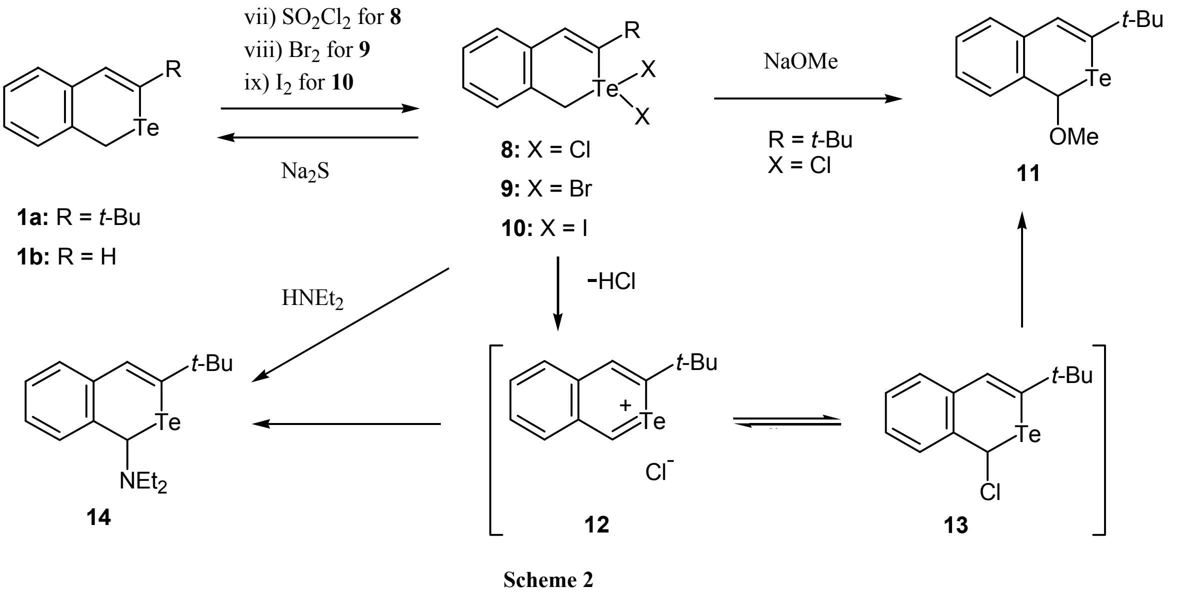
Several types of isotellurochromenium salts and related compounds (**2-7**) were newly prepared from the isotellurochromenes (**1**) as shown in Scheme 1. The reaction of the isotellurochromenes **1** with methyl iodide and 1.1 equiv. of silver tetrafluoroborate ($AgBF_4$) in CH_2Cl_2 at room temperature gave the 2-methylisotellurochromenium tetrafluoroborates (**2a, 2b**) in 84 and 75% yields, respectively. The treatment of the isotellurochromenes (**1**) with methyl trifluoromethanesulfonate (triflate, OTf^-) or ethoxycarbonylmethyl triflate[14] in acetonitrile at 0 °C similarly afforded the corresponding triflates **3a, 3b, 4a**, **4b** in high yields. 2-Phenylisotellurochromenium salt (**5**) was also synthesized from the isotellurochromene (**1**). The phenylation reaction of **1** was conducted using the diphenyliodonium triflate and copper (II) diacetate.[15] Heating at 140 °C of a mixture of 3-*tert*-butylisotellurochromene (**1a**), diphenyliodonium triflate and a catalytic amount of copper (II) diacetate produced 2-phenylisotellurochromenium triflate (**5a**) in 75% yield. However, the reaction of 3-unsubstituted isochromene (**1b**) under the same conditions gave a complex mixture; no 2-phenylisotellurochromenium triflate (**5b**) was produced. When the 3-alkylisotellurochlomenes were phenylated with the same reagents, no 2-phenylchromenium salts were obtained. The 2-methylisotellurochromenium sulfonates (**6a, 6b**) were produced by the heating of **1a, b** and methyl *p*-toluenesulfonate (methyl tosylate, MeOTs) at 60 °C under solvent free-conditions in 98 and 57% yields, respectively. Methyl methanesulfonate (methyl mesylate, MeOMs) also reacted with **1** to give the mesylates (**7a, 7b**) in a similar manner.



Scheme 1

2. Preparation of 2,2-dihalogenoisotellurochromenes

The treatment of the isoselenochromene with sulfuryl chloride is known[16] to give the 2-benzoselenopyrylium chloride *via* the unstable dehydrochlorination of the dichloro-adduct. In contrast, both the cyclic and acyclic tellurides react with sulfuryl chloride to afford the essential corresponding dichlorotellurides, which were stable enough to be isolated. Therefore, the chlorination of the isotellurochromenes **1** using sulfuryl chloride was carried out. The reaction of 3-*tert*-butylisotellurochromene (**1a**) with a small excess of sulfuryl chloride in hexane at 0 ˚C produced 2,2-dichloro-3-*tert*-butylisotellurochromene (**8a**) in almost quantitative yields as stable prisms. 2,2-Dibromo-3-*tert*-butylisotellurochromene (**9a**) and 2,2-diiodo-3-*tert*-butylisotellurochromene (**10a**) were also prepared by the reaction of the 3-*tert*-butylisotellurochromenes (**1a**) with bromine and iodine, respectively. 3-Unsubstituted dihalogenoisotellurochromenes (**8-10b**) were also obtained under similar conditions in good yields. The obtained compounds **2-10** in this way were thermally and photochemically quite stable crystals except **4b**. The results of these derivatives **2-10** are listed in Table 1.



Scheme 2

Table 1. Preparation of 2-substituted isotellurochomenium salt derivatives **2-10**

Product	R	X	Y	Yield (%)	Appearance, mp (°C)
2a	*t*-Bu	BF_4	Me	84	colorless prisms, 222-223
2b	H	BF_4	Me	76	colorless prisms, 129-130
3a	*t*-Bu	OTf	Me	86	colorless prisms, 110-112
3b	H	OTf	Me	68	colorless prisms, 113-114
4a	*t*-Bu	OTf	CH_2CO_2Et	98	colorless prisms, 179-181
4b	H	OTf	CH_2CO_2Et	58	colorless oil
5a	*t*-Bu	OTf	Ph	74	yellow prisms, 183-185
6a	*t*-Bu	OTs	Me	98	colorless prisms, 159-160
6b	H	OTs	Me	57	colorless prisms, 135-136
7a	*t*-Bu	OMs	Me	94	colorless prisms, 98-99
7b	H	OMs	Me	43	colorless prisms, 177-179
8a	*t*-Bu	Cl	-	100	colorless prisms, 188-190
8b	H	Cl	-	96	colorless prisms, 183-185
9a	*t*-Bu	Br	-	100	pale yellow prisms, 1146-147
9b	H	Br	-	88	colorless prisms, 159-164
10a	*t*-Bu	I	-	100	pale yellow prisms, 134-136
10b	H	I	-	81	pale yellow prisms, 197-200

Next, we examined some reactions of the halogenoisochromenes (**8-10**). The dichloroisotellurochromenes (**8a, b**) were quantitatively dechlorinated under treatment with sodium sulfide in hexane at room temperature reverting to the isotellurochromenes (**1a, b**). A similar dehalogenation of the dibromo **9a, b** and diiodo derivatives **10a, b** also smoothly proceeded to afford **1a, b**. The treatment of **8a** with NaOMe in MeOH gave the 1-methoxyisotellurochromene (**11**) in 98% yield. This reaction would proceed *via* the intermediates, telluropyrylium chloride (**12**) or 1-chloroisotellurochromene (**13**), generated by the dehydrochlorination from **8a**, following by the nucleophilic attacking of the methoxide ion at the C-1 position affording the 1-methoxyisotellurochromene (**11**). The 1-methoxyisochromene (**11**) was also obtained from the dibromo (**9a**) and diiodoisochromemes (**10a**) in high yields. When **8a** and **9a** were treated with diethylamine in benzene at 50 ˚C, the reaction mixtures immediately became yellow, and the starting materials disappeared. The 1-(diethylamino)isotellurochromene (**14**) was obtained in high yields. However, **14** was not obtained from **10a**. Compounds **11** and **14** were identical to the authentic samples, which were previously prepared by the reaction of the 2-benzotelluropyrylium salt with NaOMe or diethylamine.

Table 2. ^{1}H-NMR ($CDCl_3$) data of isotellurochromenium salts derivatives **2-7**

Compd.	Y	Ph-H	4-H	1-H_2	R (*t*-Bu or 3-H)	X^-
2a	2.09 (3H, s) Me	7.20-7.58 (4H, m)	6.66 (1H, s)	4.40, 4.67 (each 1H, d[a])	1.36 (9H, s)	BF_4
2b	2.17 (3H, s) Me	7.23-7.50 (4H, m)	6.65 (1H, d[b])	4.06, 4.37 (each 1H, d[a])	7.06 (1H, d, *J* = 10 Hz)	BF_4
3a	2.08 (3H, s) Me	7.21-7.53 (4H, m)	6.67 (1H, s)	4.42, 4.61 (each 1H, d[a])	1.35 (9H, s)	OTf
3b	2.13 (3H, s) Me	7.15-7.50 (4H, m)	6.67 (1H, d[b])	4.00, 4.34 (each 1H, d[a])	7.03 (1H, d, *J* = 10 Hz)	OTf
4a	3.26, 3.75 (each 1H, d, *J* = 14 Hz)[c] 1.22, 4.10 (3H, t, 2H, q, *J* = 7 Hz)[d]	7.19-7.49 (4H, m)	6.75 (1H, s)	4.48, 4.72, (each 1H, d[a])	1.39 (9H, s)	OTf
4b	3.58, 3.60 (each 1H, d, *J* = 14 Hz)[c] 1.23, 4.12 (3H, t, 2H, q, *J* = 7 Hz)[d]	7.22-7.55 (4H, m)	6.64 (1H, d[b])	4.13, 4.50 (each 1H, s)	7.12 (1H, d, *J* = 10 Hz)	OTf
5a	6.78-7.57 (10H, m) Ph			4.59, 4.81 (each 1H, d[a])	1.39 (9H, s)	OTf
6a	2.15 (3H, s) Me	7.10-7.56 (6H, m)	6.65 (1H, s)	4.46, 4.73 (each 1H, d[a])	1.31 (9H, s)	2.36 (3H, s, Ar-Me) 7.82 (2H, d, *J* = 8 Hz) OTs
6b	2.24 (3H, s) Me	7.16-7.44 (4H, m)	6.73 (1H, d[b])	4.05, 4.10 (each 1H, d[a])	6.96 (1H, d, *J* = 10 Hz)	2.36 (3H, s, Ar-Me) 7.18, 7.76 (each 2H, d, *J* = 8 Hz) OTs
7a	2.12 (3H, s) Me	7.21-7.51 (4H, m)	6.66 (1H, s)	4.45, 4.64 (each 1H, d[a])	1.33 (9H, s)	2.83 (3H,s) OMs
7b	2.20 (3H, s) Me	7.19-7.63 (4H, m)	6.78 (1H, d[b])	4.04, 4.23 (each 1H, d[a])	7.03 (1H, d, *J* = 10 Hz)	2.74 (3H, s) OMs

[a] *J* = 14 Hz, [b] *J* = 10 Hz, [c] CH_2, [d] CO_2Et

2. 3. Structures of isotellurochromenium salts

The structures of these telluronium salts (**2-7**) were mainly characterized on the basis of their ^{1}H-NMR, MS and elemental analyses. Their ^{1}H-NMR data are listed in Table 2. The MS spectra of the isotelluronium tetrafluoroborates (**2**) and triflates (**3-5**) did not display any molecular ion peaks (M^+), but showed only fragment ion peaks arising from the cationic isochromenium moieties. Two 1-benzylic proton signals of **2-5** appeared as a pair of doublets (coupling constant, J = 14 Hz) at δ *ca*. 4.0-4.9 in the ^{1}H-NMR spectra (in $CDCl_3$). Similarly, the MS spectra of the tosylates (**6**) and the mesylates (**7**) did not show the M^+, and the ^{1}H-NMR spectra (in $CDCl_3$) of **6** and **7** had a pair of doublets at δ *ca*. 4.0-4.8 assigned to 1-benzylic protons with geminal coupling (J = 14 Hz). Similar ^{1}H-NMR spectral data in CD_3CN were also obtained. In all cases, the olefinic protons at the C-4 are observed as a singlet at 6.6-6.8. These spectral data suggest that the tetrafluoroborates (**2**), triflates (**3-5**), tosylates (**6**) and mesylates (**7**) are salts containing a tellurium cation.

15: X = BF_4
16: X = OTf

17: X = OTs
18: X = OMs

Figure 1

On the other hand, the spectroscopic properties of the isoselenochromanium salts, six-membered selenium-containing heterocycles, have been reported by Hori and Kataoka *et al.*,[8] but without X-ray analysis in 1990. They described that the tetrafluoroborate **15** and triflate **16** were selenium salts; their EI-MS did not show M^+, but showed only fragment ion peaks arising from the cationic moieties. On the contrary, the MS spectra of the 2-methylisoselenochromanium tosylate (**17**) and mesylate (**18**) showed the M^+. Hence, they concluded that the tosylate **17** and mesylate **18** had the selenurane structures with four covalent bonds. Therefore, an X-ray crystallographic analysis of the isotelluronium tosylates (**6**) was carried out in order to confirm the structure around the tellurium atom in this study. Fig. 2 shows the molecular structure of the 3-*tert*-butyl derivative (**6a**). Table 3 lists the selected interatomic distances, angles and torsional angles of **6a**. For the crystallographic structure of **6a**, the cationic tellurium containing a six-membered ring has twisted envelope skeletons. The bond lengths (Te-C, 2.122 and 2.144 Å) are slightly shorter than the observed value in the neutral telluracyclohexane skeletons (av. 2.157 Å) and this may be caused by the cationic attractive effect on the tellurium center, although the C-Te-C angle (89.8 °) in the heterocycle almost shows the expected value for the neutral telluracyclohexane skeletons (av. 89.3 °)[17] The cationic tellurium center is weakly coordinated by the oxygen atoms in the counter anionic tosylate (2.815 and 2.944 Å), and such weak interactions or secondary bonds have been reported between the chalcogen onium and atoms in an anion in the solid state.[18]

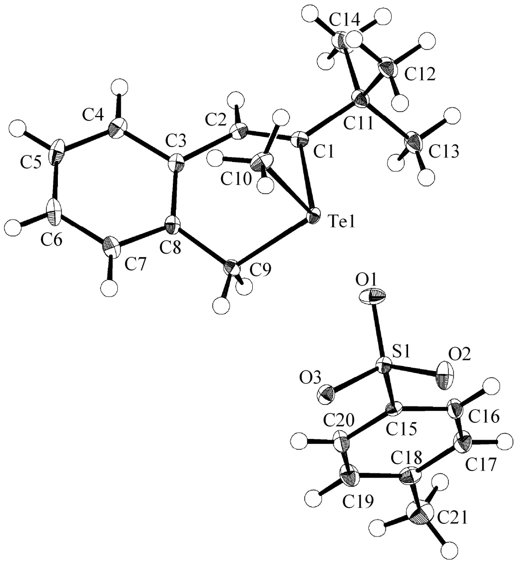


Figure 2. ORTEP drawing of **6a** with atomic numbering scheme for selected atoms (50% probability thermal level)

Table 3. Selected bond lengths (Å) and angles (deg) of **6a**

Te1–C1	2.144(2)	C1–C2	1.341(2)
Te1–C9	2.122(2)	C2–C3	1.472(2)
Te1–C10	2.125(2)	C3–C8	1.408(2)
		C8–C9	1.496(2)
C1–Te1–C9	89.84(6)	C1–C2–C3	129.3(1)
C1–Te1–C10	93.39(6)	C2–C3–C8	123.7(1)
C9–Te1–C10	97.88(6)	C3–C8–C9	121.4(5)
C2–C1–C11	125.9(1)	C8–C9–Te1	111.7(4)
Te1–C1–C2	118.2(1)		

4. Structures of the dihalogenoisotellurochromenes

The ^{1}H-NMR data of the dihalogenoisotellurochromenes (**8-10**) are listed in Table 4. The M^+ of the 2,2-dichloroisotellurochromenes (**8**) were observed in the EI-MS spectra, but very weak. The EI-MS of the 2,2-dibromoisotellurochromenes (**9**) did not show the M^+, but showed a fragment ion peak assigned to M^+-Br. Neither M^+ nor M^+-I of the 2,2-diiodoisotellurochromenes (**10**) were observed; only fragment ion peaks due to I_2 from the M^+. However, the elemental analyses of these dihalogenoisotellurochromenes (**2-4**) gave satisfactory results. The ^{1}H-NMR spectra of **8-10** in $CDCl_3$ showed two 1-benzylic proton signals as a singlet peak at δ 4.92–5.15. These findings suggest that the 2,2-dihalogenoisotellurochromenes **8-10** take the tellurane structures, which share the trigonal-bipyramidal geometry of the hypervalent tellulium compounds having two equal tellurium-halogen σ covalent bonds. The molecular structure of **8a** was finally determined by X-ray crystallographic analysis (Fig. 3). Table 5 lists the selected interatomic distances, angles and torsional angles of **8a**.

Table 4. ^{1}H-NMR ($CDCl_3$) data of 2,2-dihalogenoisotellurochromenes **8-10**

Compd.	Ph-H	4-H	1-H_2	R (*t*-Bu or 3-H)	X
8a	7.26-7.40 (4H, m)	6.74 (1H, s)	5.02 (2H, s)	1.52 (9H, s)	Cl
8b	7.23-7.48 (4H, m)	6.88 (1H, d, *J* = 10 Hz)	4.92 (2H, s)	7.16 (1H, d, *J* = 10 Hz)	Cl
9a	7.26-7.40 (4H, m)	6.68 (1H, s)	5.15 (2H, s)	1.54 (9H, s)	Br
9b	7.26-7.42 (4H, m)	6.80 (1H, d, *J* = 10 Hz)	5.02 (2H, s)	7.15 (1H, d, *J* = 10 Hz)	Br
10a	7.26-7.40 (4H, m)	6.68 (1H, s)	5.15 (2H, s)	1.54 (9H, s)	I
10b	7.19-7.50 (4H, m)	6.75 (1H, d, *J* = 10 Hz)	4.95 (2H, s)	7.09 (1H, d, *J* = 10 Hz)	I

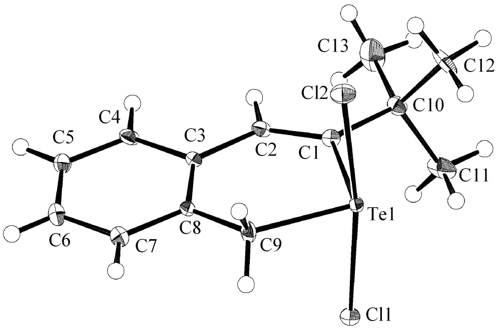


Figure 3. ORTEP drawing of **8a** with atomic numbering scheme for selected atoms (50% probability thermal level)

Table 5. Selected bond lengths (Å) and angles (deg) of **8a**

Te1–C1	2.114(5)	C1–C2	1.329(8)
Te1–C9	2.116(5)	C2–C3	1.468(7)
Te1–Cl1	2.541(1)	C3–C8	C3–C8
Te1–Cl2	2.505(2)	C8–C9	1.509(8)
C1–Te1–C9	97.7(2)	Te1–C1–C2	118.4(4)
C1–Te1–Cl2	88.10(15)	C1–C2–C3	132.6(5)
C9–Te1–Cl2	87.40(18)	C2–C3–C8	126.6(5)
C1–Te1–Cl1	89.43(15)	C3–C8–C9	125.8(5)
C9–Te1–Cl1	85.24(18)	C8–C9–Te1	118.1(4)
Cl2–Te1–Cl1	171.85(5)		

The tellurium containing six membered ring in **8a** has an almost planar structure. The tellurium environment of **8a** has a pseudo-trigonal bipyramidal (TBP) geometry consisting of two chlorine atoms in the apical positions and two equatorial carbon atoms. The bond angle of Cl-Te-Cl (171.9 °) indicates repulsions between the Te-Cl bonds and lone pair electrons on the Te atom. This bond angle and the bond lengths of Te-Cl (2.505 and 2.541 Å) are comparable to those observed in the $R_2Te^{IV}Cl_2$ compounds where the corresponding averaged bond angle and length are 174.9 ° and 2.508 Å, respectively.[19]

CONCLUSION

Several types of isotellurochromenium salts having a methyl, phenyl and ethoxycarbonyl group on the tellurium atom at the C-2 position, and the 2,2-dihalogenoisotellurochromenes were easily prepared from the parent isotellurochromenes in good to high yields in one-pot. BF_4^-, OTf^-, OTs^- and OMs^- were selected as the counter anion of the salts. The ^{1}H-NMR spectra of these derivatives were described and the X-ray crystallographic analyses were also reported. As a consequence, the 2-methylisotellurochromenium tosylate was found to have a telluronium salt structure with a tosylate as the counter anion.

EXPERIMENTAL

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Horiba FT-720 spectrometer. Mass spectra (MS) and HRMS were recorded on a JEOL JMS-DX300 instrument. NMR spectra were determined with a JEOL EX-90A (90 MHz) or a JEOL JNM-GSX 400 (400 MHz) spectrometer in $CDCl_3$ or CD_3CN using tetramethylsilane as internal standard and *J* values are given in Hz. Microanalyses were performed in the Microanalytical Laboratory in this Faculty.

Preparation of 2-methylisotellurochromenium tetrafluoroborate (2)

Silver tetrafluoroborate (220 mg, 1.1 mmol) was added to a mixture of isotellurochromene (**1**, 1.0 mmol) and MeI (1.0 mL) at 0 °C, and the mixture was stirred overnight at room temperature. Excess MeI was evaporated, the residue was triturated and extracted with MeCN, and filtrated to remove silver iodide. The filtrate was evaporated, and the residual solid was recrystallized from MeCN-Et_2O to give **2**.

3-*tert*-Butyl-2-methylisotellurochromenium Tetrafluoroborate (2a)

EIMS (relative intensity) *m/z*: 317 [$(M-BF_4)^+$, 17], 302 (100), 300 (92), 157 (100), 115 (48). IR (KBr) (cm^{-1}): 1083 (BF_4). *Anal.* Calcd for $C_{14}H_{19}BF_4Te$: C, 41.86; H, 4.77. Found: C, 41.94; H, 4.57.

2-Methylisotellurochromenium Tetrafluoroborate (2b)

EIMS (relative intensity) *m/z*: 260 [$(M-HBF_4)^+$, 5], 246 (45), 244 (42), 115 (100). IR (KBr) (cm^{-1}): 1097 (BF_4). *Anal.* Calcd for $C_{10}H_{11}BF_4Te$: C, 34.75; H, 3.21. Found: C, 34.64; H, 3.21.

Preparation of 2-methylisotellurochromenium triflate (3)

Methyl triflate (165 mg, 1.0 mmol) was added to isotellurochromene (**1**, 1.0 mmol) at 0 °C, and the mixture was stirred for 2-3 h at room temperature. The oily residue was washed with a mixture of Et_2O and hexane (1:1), and the residual solid was recrystallized from MeCN-Et_2O to give **3**.

3-*tert*-Butyl-2-methylisotellurochromenium Triflate (3a)

EIMS (relative intensity) *m/z*: 317 $[(M\text{-}OTf)^+$, 100], 315 (92), 302 (33), 157 (63). IR (KBr) (cm^{-1}): 1161, 1248, 1281 (OTf). *Anal.* Calcd for $C_{15}H_{19}O_3F_3STe$: C, 38.83; H, 4.13. Found: C, 38.63; H, 4.01.

2-Methylisotellurochromenium Triflate (3b)

EIMS (relative intensity) *m/z*: 261 $[(M\text{-}OTf)^+$, 38], 259 (30), 246 (35), 115 (100). IR (KBr) (cm^{-1}): 1163, 1250, 1273 (OTf). *Anal.* Calcd for $C_{11}H_{11}O_3F_3STe$: C, 32.39; H, 2.72. Found: C, 32.38; H, 2.71.

Preparation of 2-(ethoxycarbonylmethyl)isotellurochromenium triflate (4)

Ethoxycarbonylmethyl triflate (295 mg, 1.25 mmol) was added to a solution of isotellurochromene (**1**, 1.0 mmol) in MeCN (5 mL) at 0 °C. The mixture was stirred overnight at room temperature and then evaporated. The oily residue was washed with hexane, and the residual solid was recrystallized from CH_2Cl_2-hexane to give **4**.

3-*tert*-Butyl-2-(ethoxycarbonylmethyl)isotellurochromenium Triflate (4a)

EIMS (relative intensity) *m/z*: 302 $[(M\text{-}OTf\text{-}CH_2COOC_2H_5)^+$, 100], 157 (85). IR (KBr) (cm^{-1}): 1724 (C=O), 1158, 1231, 1282 (OTf). *Anal.* Calcd for $C_{18}H_{23}O_5F_3STe$: C, 40.33; H, 4.32. Found: C, 40.39; H, 4.20.

2-(Ethoxycarbonylmethyl)isotellurochromenium Triflate (4b)

EIMS (relative intensity) *m/z*: 333 $[(M\text{-}OTf)^+$, 35], 246 (37), 244 (35), 115 (100). IR (KBr) (cm^{-1}): 1716 (C=O), 1169, 1250, 1277 (OTf). *Anal.* Calcd for $C_{14}H_{15}O_5F_3STe$: C, 35.04; H, 3.15. Found: C, 34.89; H, 2.99.

Preparation of 3-*tert*-butyl-2-phenylisotellurochromenium triflate (5a)

A mixture of isotellurochromene (**1a**, 302 mg, 1.0 mmol) and diphenyliodonium triflate (1.3 mmol) and copper (II) acetate (0.01 mmol) was heated with stirring at 140 ˚C for 3 h under argon atmosphere. The reaction mixture was cooled to room temperature and Et_2O (50 mL) was added. The resulting crystals were triturated, collected by filtration, and washed with Et_2O to remove iodobenzene and the by-products. The crude crystals were recrystallized from $CHCl_3$- Et_2O.

EIMS (relative intensity) *m/z*: 279 $[(M\text{-}OTf)^+$, 100], 302 (12), 157 (71). IR (KBr) (cm^{-1}): 1153, 1221, 1258, 1279 (OTf). *Anal.* Calcd for $C_{20}H_{21}O_3F_3STe$: C, 45.66; H, 4.02. Found: C, 45.44; H, 4.16.

Preparation of 2-methylisotellurochromenium tosylate (6)

A mixture of isotellurochromene (**1,** 1.0 mmol) and methyl *p*-tosylate (186 mg, 1.0 mmol) was heated at 60 °C under argon atmosphere with stirring for 2 h. After cooling, the solid was recrystallized from CH_2Cl_2-Et_2O to give **6**.

3-*tert*-Butyl-2-methylisotellurochromenium Tosylate (6a)

FABMS (relative intensity) *m/z*: 317 [$(M\text{-}OTs)^+$, 100], 157 (45). IR (KBr) (cm^{-1}): 1180, 1216 (SO_3). *Anal.* Calcd for $C_{21}H_{26}O_3STe$: C, 51.89; H, 5.39. Found: C, 51.71; H, 5.34.

2-Methylisotellurochromenium Tosylate (6b)

FABMS (relative intensity) *m/z*: 261 [$(M\text{-}OTs)^+$, 100], 154 (85). IR (KBr) (cm^{-1}): 1164, 1215 (SO_3). *Anal.* Calcd for $C_{17}H_{18}O_3STe$: C, 47.49; H, 4.22. Found: C, 47.37; H, 4.29.

Preparation of 2-methylisotellurochromenium mesylate (7)

A mixture of isotellurochromene (**1**, 1.0 mmol) and methyl mesylate (110 mg, 1.0 mmol) was heated at 60 °C under argon atmosphere with stirring for 2 h. After cooling, the solid was recrystallized from CH_2Cl_2-Et_2O to give **7**.

3-*tert*-Butyl-2-methylisotellurochromenium Mesylate (7a)

EIMS (relative intensity) *m/z*: 317 [$(M\text{-}OMs)^+$, 10], 302 (100), 287 (28), 157 (100), 115 (48). IR (KBr) (cm^{-1}): 1194, 1205 (SO_3). *Anal.* Calcd for $C_{15}H_{22}O_3STe$: C, 43.94; H, 5.41. Found: C, 44.03; H, 5.37.

2-Methyl-2-isotellurochromenium Mesylate (7b)

EIMS (relative intensity) *m/z*: 261 [$(M\text{-}OMs)^+$, 5], 246 (55), 115 (100). IR (KBr) (cm^{-1}): 1176, 1211 (SO_3). *Anal.* Calcd for $C_{11}H_{14}O_3STe$: C, 37.33; H, 3.99. Found: C, 37.12; H, 3.84.

Preparation of 2,2-dihalogenoisotellurochromene (8-10)

1.05 mol Equivalent amount of SO_2Cl_2 (142 mg), Br_2 (170 mg) or I_2 (267 mg) was added to a solution of isotellurochromene (**1**, 1.0 mmol) in hexane (20 mL) with stirring in an ice bath, and the mixture was stirred for 30 min at 0-5 °C. The resulting precipitate was collected by filtration, washed with hexane, and recrystallized from benzene-hexane to give **8-10**.

3-*tert*-Butyl-2,2-dichloroisotellurochromene (8a)

EIMS (relative intensity) *m/z*: 376, 374, 372 (M^+, 1, 3, 1), 337 (10), 302 (76), 300 (70), 157 (100). EIHRMS *m/z*: 371.9688 (Calc. for $C_{13}H_{16}{}^{35}Cl_2{}^{130}Te$: 371.9672). *Anal.* Calcd for $C_{13}H_{16}Cl_2Te$: C, 42.11; H, 4.35. Found: C, 42.26; H, 4.28.

2,2-Dichloroisotellurochromene (8b)

EIMS (relative intensity) *m/z*: 316 (M^+, 1), 281 (6), 246 (36), 244 (34), 115 (100). EIHRMS *m/z*: 315.9059 (Calc. for $C_9H_8{}^{35}Cl_2{}^{130}Te$: 315.9065). *Anal.* Calcd for $C_9H_8Cl_2Te$: C, 34.35; H, 2.56. Found: C, 34.30; H, 2.55.

3- 2,2-Dibromo- *tert*-butyl-isotellurochromene (9a)

EIMS (relative intensity) *m/z*: 381 [(M-Br)$^+$, 76], 379 (59), 302 (100), 157 (84). EIHRMS *m/z*: 380.9488 (Calc. for $C_{13}H_{16}{}^{79}Br^{130}Te$: 380.9498). *Ana*l. Calcd for $C_{13}H_{16}Br_2Te$: C, 33.97; H, 3.51. Found: C, 34.01; H, 3.43.

2,2-Dibromoisotellurochromene (9b)

EIMS (relative intensity) *m/z*: 325 [(M-Br)$^+$, 20], 246 (35), 244 (33), 115 (100). EIHRMS *m/z*: 324.8869 (Calc. for $C_9H_8{}^{79}Br^{130}Te$: 324.8872). *Anal.* Calcd for $C_9H_8Br_2Te$: C, 26.79; H, 2.00. Found: C, 26.89; H, 1.98.

3-*tert*-Butyl-2,2-diiodoisotellurochromene (10a)

EIMS (relative intensity) *m/z*: 302 [(M-I$_2$)$^+$, 55], 300 (51), 254 (100), 157 (54). EIHRMS *m/z*: 302.0301 (Calc. for $C_{13}H_{16}{}^{130}Te$: 302.0314). *Anal.* Calcd for $C_{13}H_{16}I_2Te$: C, 28.20; H, 2.91. Found: C, 28.03; H, 2.79.

2,2-Diiodoisotellurochromene (10b)

EIMS (relative intensity) *m/z*: 254 (I$_2$, 100), 246 [(M-I$_2$)$^+$, 35), 115 (72). EIHRMS *m/z*: 245.9672 (Calc. for $C_9H_8{}^{130}Te$: 245.9688). *Anal.* Calcd for $C_9H_8I_2Te$: C, 21.72; H, 1.62. Found: C, 21.58; H, 1.58%.

X-Ray structure determination

Single crystals of **6a** were obtained from solution of acetonitrile after slow evaporation of the solvent at room temperature, **8a** from solutions of *n*-hexane/dichloromethane. Diffraction data were collected on a Bruker Apex-II CCD diffractometer equipped with a graphite monochromated MoKα radiation source ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97),[20] and refined by full-matrix least-square methods on *F*2 for all reflections (SHELXL-97)[21] with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic.

For **6a**, the structure analysis is based on 4449 observed reflections with $I > 2.00\ \sigma(I)$ and 240 variable parameters; colorless needles, 113 K, *triclinic*, space group *P*-1, $a = 9.6655(2)$ Å, $b = 10.5362(6)$ Å, $c = 10.9056(1)$ Å, $\alpha = 80.724(7)°$, $\beta = 68.336(6)°$, $\gamma = 89.062(7)°$, $V = 1017.54(7)$ Å^3, $Z = 2$, $R = 0.0171$, $R_w = 0.0435$*GOF* = 1.056.

For **8a**, the structure analysis is based on 2822 observed reflections with $I > 2.00\ \sigma(I)$ and 163 variable parameters; yellow needles, 196 K, *orthorhombic*, space group *P*bca, $a = 8.3371(2)$ Å, $b = 33.438(1)$ Å, $c = 9.861(2)$ Å, $V = 2758.79(12)$ Å^3, $Z = 8$, $R = 0.0324$, $R_w = 0.0959$, *GOF* = 1.515.

CCDC-742488 for **6a** and CCDC-742489 for **8a** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.

Dehalogenation of 8-10 with Sodium Sulfide

General Procedure: A 2% aqueous Na_2S solution (5 mL) was added to a solution of **8a** (20 mg) in hexane with vigorous stirring in an ice bath. After stirring for 10 min, water (10 mL) was added to the reaction mixture, and the whole was extracted with CH_2Cl_2 (20 mL x 2). The combined extract was dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel using hexane-CH_2Cl_2 to give isotellurochromene (**1**).

From **8a**: 98% yield. From **8b**: 92% yield. From **9a**: 97% yield. From **9b**: 95% yield. From **10a**: 98% yield. From **10b**: 94% yield.

Reaction of 8-10a with NaOMe

28% NaOMe in MeOH (2 mL) was added to a solution of **8a** (112 mg, 0.3 mmol) in MeOH (10 mL) at 0 °C. The reaction mixture was stirred for 15 min and then poured into ice-water. The aqueous mixture was extracted with CH_2Cl_2 (20 mL x 3), the organic layer was washed with brine (30 mL x 3) and dried over $MgSO_4$. The solvent was evaporated to give the 1-methoxy-1*H*-isotellurochromene (**11**) in a nearly pure form as colorless oil. This compound was identical with an authentic sample in terms of ^{1}H-NMR, IR and MS.

From **8a**: 97% yield. From **9a**: 97% yield. From **10a**: 98% yield.

Reaction of 8-10a with $NHEt_2$

Diethylamine (0.6 mL) was added slowly to a suspended mixture of **8a** (112 mg, 0.3 mmol) in benzene (6 ml) at room temperature under argon atmosphere. The mixture was stirred at 50 ˚C for 1 h, and then extracted with benzene (20 mL x 3). Benzene layer was washed with brine (30 mL x 3) and dried ($MgSO_4$), and evaporated to give the 1-diethylamino-1*H*-isotellurochromene (**14**) in a nearly pure form as colorless oil. This compound was also identical with an authentic sample in terms of ^{1}H-NMR, IR and MS.

From **8a**: 95% yield. From **9a**: 93% yield.

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