Studies on Tellurium-Containing Heterocycles. Part 20.[1] Reactions of 2-Benzoselenopyrylium Salts and 2-Benzotelluropyrylium Salts with Nucleophiles: Formation of 1-Functionalized 1*H*-Isoselenochromenes and 1*H*-Isotellurochromenes

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The reactions of the 2-benzoselenopyrylium (1A) and 2-benzotelluropyrylium cations (1B) with a variety of nucleophiles have been investigated. $LiAlH_4$, sodium alkoxide (NaOMe, NaO*i*-Pr and NaO*t*-Bu), diethylamine, *n*-butylamine and acetone reacted with 1 to give the 1*H*-isochromenes (2) and the corresponding 1-substituted products (4—9) under mild conditions in almost good to high yields. The 1-alkyl(phenyl)isoselenochromenes (10—13) and 1-benzylisochromenes (18A, 18B), which were produced by the reaction of the salts 1 with Grignard reagents, were converted to the corresponding 1,3-disubstituted 2-benzopyrylium salts (14—17, 19) by treatment with triphenylcarbenium tetrafluoroborate (Ph_3C^+ BF_4^-), respectively. The 1-benzylselenopyrylium salts (19A) and 1-benzyltelluropyrylium salts (19B) exist in the solvent as an equilibrium mixture of the salts (19) and the corresponding (*Z*)-benzylidene compounds (20).

Key words 2-benzoselenopyrylium salt; 2-benzotelluropyrylium salt; isoselenochromene; isotellurochromene; nucleophile

Recently, the chemistry of the selenopyrylium[2—4] and telluropyrylium salts,[2—5] six-membered cationic heteroaromatics containing a selenium or tellurium atom, in both fields of organic synthesis and the chemical transformation of organotellurium and organoselenium compounds, has attracted considerable attention. Both of the monocyclic pyrylium[6,7] and 1-benzopyrylium salts[8—10] containing these atoms have been prepared, and the chemistry of these compounds has been reviewed. We have also previously reported the practical and facile preparation[11—13] and the reactions[11,14,15] of these 1-benzopyrylium salts. More recently, we succeeded in preparing[16] the stable 2-benzotelluropyrylium[17] and 2-benzoselenopyrylium salts,[18] structural isomers of them; the former is a previously unknown heterocyclic ring system. Therefore, this paper deals with the results of the examination of the reactivity of these novel 2-benzopyrylium salts with various nucleophiles using the stable compounds, 3-*tert*-butyl and (or) 3-unsubstituted derivatives as easily available pyrylium salts. The differences in the reactivity of these pyrylium salts containing a tellurium or selenium atom have received most of our attention thus far.

Results and Discussion

Reduction of Pyrylium Salts The reductions of the monocyclic chalcogenopyrylium ions by hydride donors such as $LiAlH_4$,[19,20] $NaBH_4$,[21] $LiBH_4$[22] and diisobutylaluminum hydride (DIBAL-H)[23] were reported. In all cases, the major products are 4*H*-pyrans. The one-electron reduction of them when treated with zinc dust[24—26] in a degassed aprotic solvent gives the bichalcogenopyran derivatives *via* the pyranyl radical intermediates. We have previously described that the $LiAlH_4$ reduction of the 1-benzotelluropyrylium salts[11] and 1-benzoselenopyrylium salts,[14] the regioisomers of the title compounds, afforded a mixture of the corresponding 2*H*- and 4*H*-chromenes, respectively; the latter was the major product. In order to compare these behaviors, we first examined the hydride reduction of the 2-benzopyrylium salts (**1**). The reduction of **1A** and **1B** with $LiAlH_4$ in diethyl ether at 0 °C afforded the 1*H*-isoselenochromenes (**2A**) and 1*H*-isotellurochoromenes (**2B**) in moderate yields as the sole products, respectively. The use of THF as a solvent almost gave similar results. The pyrylium salts (**1**) were also reduced by DIBAL-H to give the 1*H*-isochromenes (**2**) in quantitative yields. These compounds (**2**) were identical with the authentic samples,[16] which were the precursors for the synthesis of the corresponding pyrylium salts (**1A**) and (**1B**). The 3-*tert*-butyl-2-benzopyrylium salts (**1Aa**) and (**1Ba**) reacted with excess zinc dust in acetonitrile at 0 °C under an argon atmosphere to give 1,1′-bis(*tert*-butylisochromenyl) (**3Aa**) and (**3Ba**) in 18 and 15% yield as the sole characterized products, respectively. The MS spectrum of compound **3Aa** suggested the diselenide molecular formula of $C_{26}H_{30}Se_2$ as it measured a molecular ion at $m/z=502$ (^{80}Se) and the expected isotope pattern for Se_2. The base peak was $m/z=251$, which was a half of the molecular ion. In addition the HR-MS of **3Aa** showed the exact molecular formula. There was no characteristic absorption in the IR spectrum. **3Aa** and **3Ba** were also obtained by the catalytic hydrogenation of **1a** using 5% Pd–C in THF in *ca.* 25% yields. These bisisochromenyl compounds (**3**) would be produced by the homo-coupling of the radical intermediates.[24—26]

Reaction of Pyrylium Salts with Nucleophiles We have recently found that both the 1-benzotelluropyrylium[11] and 1-benzoselenopyrylium salts[14] were attacked by a methoxide ion in MeOH to form the corresponding 4-methoxy-4*H*-chromenes as the major products in high yields. Although the telluropyrylium salts did not react with a secondary or tertiary alkoxide in the corresponding alcohol to give any characterizable products, the unsubstituted 1-benzoselenopyrylium salts[14] reacted with NaO*i*-Pr and KO*t*-Bu to afford the corresponding the 2-alkoxy-2*H*-selenochromenes in good yields. Furthermore, the NaO*i*-Pr ion attacked the C-4 position of the 2-substituted selenopyrylium salts to give the 4-isopropoxy-4*H*-selenochromenes.[14] Thus,

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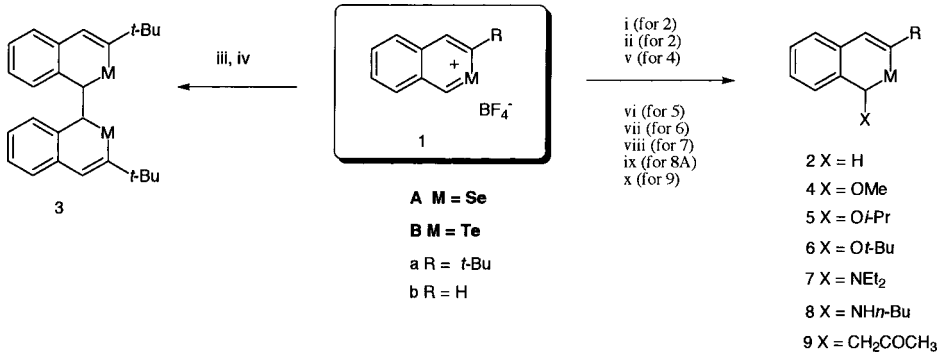

Reagents and conditions: i, $LiAlH_4$, Et_2O, 0 °C, ii, DIBAL-H, THF, −20 °C, iii, Zn dust, MeCN, 0 °C to room temp., iv, H_2, Pd–C, THF, room temp., v, NaOMe, MeOH, room temp., vi, NaO*i*-Pr, *i*-PrOH, room temp., vii, NaO*t*-Bu, *t*-BuOH, room temp., viii, $NHEt_2$, benzene, room temp., ix, NH_2 *n*-Bu, benzene, room temp., x, MeCOMe, room temp.

Chart 1

we examined the reactivities of the 2-benzoselenopyrylium (**1A**) and 2-benzotelluropyrylium salts (**1B**) towards primary, secondary and tertiary alkoxide ions. The reaction of the salts **1** with NaOMe in MeOH at room temperature resulted in the nucleophilic addition at the C-1 position on the hetero cation ring to give the desired 1-methoxy-1*H*-isochromenes (**4Aa**, **4Ab**, **4Ba**) in very high yields as the sole products except for the unsubstituted telluropyrylium salt (**1Bb**). The treatment of **1** with NaO*i*-Pr also produced the 1-isopropoxy-1*H*-isochromenes (**5**) in almost quantitative yields. Moreover, the nucleophilic attack of the tertiary butoxide ion at the same position was carried out to yield only the 1-*tert*-butoxy-1*H*-isoselenochromenes (**6Aa**, **6Ab**) in 33 and 10% yields, respectively. These facts suggest that the C-1 position on the 2-benzoseleno- and 2-benzotelluropyrylium cation ring has a higher reactivity than that of the C-4 position of the 1-benzopyrylium ring as might have been expected. For the reaction with alkoxide anions, the 3-unsubstituted telluropyrylium salt (**1Bb**) decomposed to give a complex mixture, probably due to the thermal instability of the products.

When **1** were treated with an aliphatic secondary amine, diethylamine in benzene at room temperature, the reaction mixtures immediately became yellow or orange, and the starting materials had disappeared. The corresponding 1-diethylamino-1*H*-isochoromenes (**7**) were obtained in high yields. *n*-Butylamine, a primary amine, reacted with the 2-benzoselenopyrylium salts (**1A**) to afford the desired 1-*n*-butylaminoisoselenochromenes (**8A**) in high yields. In contrast, the reaction of the 3-*tert*-butyl-telluropyrylium salt (**1Ba**) gave the complex mixture including unknown products.

Previously, we observed that both the 1-benzotelluropyrylium[11] and selenopyrylium salts[14] easily reacted with acetone in the absence of a base catalyst to afford the corresponding 1-acetonyl-1*H*-isochromene derivatives. It was also reported[27] that the 2-benzothiopyrylium salt having a benzoyl group as a strong electron-withdrawing group at the C-3 position easily reacted with acetone under similar conditions to form 1-acetonyl-3-benzoyl-1*H*-isothiochromene. These results prompted us to examine the reaction of **1** with acetone. The addition of the salts (**1**) to dry acetone at room temperature gave the 1-acetonyl-1*H*-isocheromenes (**9**). However, the yield of the products was very low except for the 1-acetonyl-3-*tert*-butyl-1*H*-isoselenocheromenes (**9Aa**).

Table 1. 1-Functionalized 1*H*-Isoselenochromenes and 1*H*-Isotellurochromenes (**4—9**)

Compd. No.	M	R	X	Yield (%)	Appearance mp/°C
4Aa	Se	*t*-Bu	OMe	98	Pale yellow oil
4Ab	Se	H	OMe	93	Yellow oil
4Ba	Te	*t*-Bu	OMe	94	Yellow prisms mp 56—58
5Aa	Se	*t*-Bu	O*i*-Pr	99	Colorless prisms mp 67—68
5Ab	Se	H	O*i*-Pr	90	Yellow oil
5Ba	Te	*t*-Bu	O*i*-Pr	96	Pale yellow prisms mp 70—71
6Aa	Se	*t*-Bu	O*t*-Bu	33	Pale yellow prisms mp 187—190
6Ab	Se	H	O*t*-Bu	10	Yellow oil
7Aa	Se	*t*-Bu	NEt_2	98	Pale yellow prisms mp 57—58
7Ab	Se	H	NEt_2	84	Yellow prisms mp 36—38
7Ba	Te	*t*-Bu	NEt_2	95	Yellow oil
8Aa	Se	*t*-Bu	NH *n*-Bu	96	Yellow oil
8Ab	Se	H	NH *n*-Bu	84	Yellow oil
9Aa	Se	*t*-Bu	CH_2COCH_3	97	Yellow oil
9Ab	Se	H	CH_2COCH_3	11	Yellow oil
9Ba	Te	*t*-Bu	CH_2COCH_3	27	Pale yellow oil

All the 1-functionalized isoselenochromenes (**3A—9A**) and isotellurochromenes (**3B—9B**) thus obtained in this way are the novel compounds except for the isochromenes (**2A**, **2B**) were mainly characterized on the basis of HR-MS and ^{1}H-NMR spectral analyses. These results and the spectral data of the products are summarized in Tables 1 and 2. Generally, the isoselenochromenes are more stable than the isotellurochromenes, and the yields of the products are higher. The 3-unsubstituted isotellurochromenes are not very stable, consequently, the 3-*tert*-butylisoselenochromenes are the most stable.

Introduction of a Carbon Functional Group at C-1 Position For the purpose to introduce a normal carbon functional group into the hetero ring of the salts (**1**), Grignard reagents are employed as the nucleophiles. The treatment of the 2-benzoselenopyrylium salts (**1A**) with Grignard reagents, such as methyl-, ethyl- and phenyl-magnesium bromide (iodide) in ether or THF at 0 °C resulted in carbon–car-

Table 2. Spectral Data for the 1-Functionalized 1*H*-Isoselenochromenes and 1*H*-Isotellurochromenes (**4—9**)

Compd. No.	M	R	X	Formula HR-MS Calcd (Found)	^{1}H-NMR (90 MHz, $CDCl_3$, *J*=Hz)				
					1-H	4-H	Ar-H	R-H	X-H
4Aa	Se	*t*-Bu	OMe	$C_{14}H_{18}OSe$ 282.0523 (282.0525)	5.76 (s)	6.90 (s)	7.2—7.3 (4H, m)	1.32 (9H, s, *t*-Bu)	3.31 (3H, s, OMe)
4Ab	Se	H	OMe	$C_{10}H_{10}OSe$ 225.9897 (225.9902)	5.77 (d, *J*=2)	7.16 (d, *J*=10)	7.2—7.4 (4H, m)	6.88 (1H, dd, *J*=10, 2, 3-H)	3.33 (3H, s, OMe)
4Ba	Te	*t*-Bu	OMe	$C_{14}H_{18}OTe$ 332.0421 (332.0412)	5.99 (s)	6.85 (s)	7.2—7.4 (4H, m)	1.30 (9H, s, *t*-Bu)	3.26 (3H, s, OMe)
5Aa	Se	*t*-Bu	O*i*-Pr	$C_{16}H_{22}OSe$ 310.0836 (310.0837)	5.84 (s)	6.90 (s)	7.2—7.3 (4H, m)	1.31 (9H, s, *t*-Bu)	1.10, 1.23 (each 3H, d, *J*=6, $OCH(C\underline{H}_3)_2$), 4.10 (1H, dq, *J*=6, 6, $OC\underline{H}(CH_3)_2$)
5Ab	Se	H	O*i*-Pr	$C_{12}H_{14}OSe$ 254.0210 (254.0202)	5.86 (d, *J*=2)	7.13 (d, *J*=10)	7.0—7.6 (4H, m)	6.83 (1H, dd, *J*=10, 2, 3-H)	1.11, 1.20 (each 3H, d, *J*=6, $OCH(C\underline{H}_3)_2$), 4.05 (1H, dq, *J*=6, 6, $OC\underline{H}(CH_3)_2$)
5Ba	Te	*t*-Bu	O*i*-Pr	$C_{16}H_{22}OTe$ 360.0734 (360.0752)	6.07 (s)	6.82 (s)	7.1—7.4 (4H, m)	1.29 (9H, s, *t*-Bu)	1.12, 1.24 (each 3H, d, *J*=6, $OCH(C\underline{H}_3)_2$), 3.92 (1H, dq, *J*=6, 6, $OC\underline{H}(CH_3)_2$)
6Aa	Se	*t*-Bu	O*t*-Bu	$C_{17}H_{24}OSe$ 324.0993 (324.0998)	6.04 (s)	6.83 (s)	7.2—7.3 (4H, m)	1.33 (9H, s, *t*-Bu)	1.30 (9H, s, O*t*-Bu)
6Ab	Se	H	O*t*-Bu	$C_{13}H_{16}OSe$ 268.0367 (268.0369)	6.10 (d, *J*=1)	7.09 (d, *J*=10)	7.2—7.4 (4H, m)	6.92 (1H, dd, *J*=10, 1, 3-H)	1.34 (9H, s, O*t*-Bu)
7Aa	Se	*t*-Bu	NEt_2	$C_{17}H_{25}NSe$ 323.1153 (323.1152)	5.75 (s)	6.71 (s)	7.1—7.3 (4H, m)	1.32 (9H, s, *t*-Bu)	1.00, 2.1—2.7 (6H, t, *J*=7, 4H, m, NEt_2)
7Ab	Se	H	NEt_2	$C_{13}H_{17}NSe$ 267.0527 (267.0522)	5.81 (br s)	6.98 (d, *J*=10)	7.0—7.3 (4H, m)	6.86 (1H, d, *J*=10, 3-H)	0.99, 2.1—2.8 (6H, t, *J*=7, 4H, m, NEt_2)
7Ba	Te	*t*-Bu	NEt_2	$C_{17}H_{25}NTe$ 373.1050 (373.1041)	5.96 (s)	6.69 (s)	7.1—7.4 (4H, m)	1.31 (9H, s, *t*-Bu)	1.04, 2.1—2.7 (6H, t, *J*=7, 4H, m, NEt_2)
8Aa	Se	*t*-Bu	NH *n*-Bu	$C_{17}H_{25}NSe$ 323.1153 (323.1147)	5.16 (s)	6.87 (s)	7.1—7.3 (4H, m)	1.30 (9H, s, *t*-Bu)	0.89, 1.2—1.4, 2.4—3.0 (3H, t, *J*=7, 4H, m, 2H, m, N *n*-Bu), 1.6 (1H, br, NH)
8Ab	Se	H	NH *n*-Bu	$C_{13}H_{17}NSe$ 267.0527 (267.0523)	5.19 (d, *J*=2)	7.03 (d, *J*=7)	7.1—7.4 (4H, m)	6.82 (1H, dd, *J*=7, 2, 3-H)	0.89, 1.2—1.6, 2.4—2.9 (3H, t, *J*=7, 4H, m, 2H, m, N *n*-Bu), 1.6 (1H, br, NH)
9Aa	Se	*t*-Bu	CH_2COCH_3	$C_{16}H_{20}OSe$ 308.0680 (308.0684)	4.40 (dd, *J*=9, 6)	6.75 (s)	7.1—7.2 (4H, m)	1.28 (9H, s, *t*-Bu)	2.03 (3H, s, $CH_2COC\underline{H}_3$) 2.80, 3.17 (1H, dd, *J*=17, 6, 1H, dd, *J*=17, 9, $C\underline{H}_2COCH_3$)
9Ab	Se	H	CH_2COCH_3	$C_{12}H_{12}OSe$ 252.0054 (252.0049)	4.39 (ddd, *J*=9, 5, 2)	6.99 (d, *J*=10)	7.1—7.4 (4H, m)	6.71 (1H, dd, *J*=10, 2, 3-H)	2.05 (3H, s, $CH_2COC\underline{H}_3$) 2.85, 3.35 (1H, dd, *J*=17, 5, 1H, dd, *J*=17, 9, $C\underline{H}_2COCH_3$)
9Ba	Te	*t*-Bu	CH_2COCH_3	$C_{16}H_{20}OTe$ 358.0577 (358.0582)	4.30 (dd, *J*=8, 7)	6.72 (s)	7.1—7.3 (4H, m)	1.27 (9H, s, *t*-Bu)	2.01 (3H, s, $CH_2COC\underline{H}_3$) 3.13, 3.38 (1H, dd, *J*=17, 7, 1H, dd, *J*=17, 8, $C\underline{H}_2COCH_3$)

bon bond formation at the C-1 position to afford the desired corresponding 1-substituted 1*H*-isoselenochromenes (**10**—**13**) in good yields. In contrast, the reaction of the telluropyrylium salt (**1Ba**) with Grignard reagents gave 1,1′-bis(*tert*-butylisotellurochromenyl) (**3B**), which was a self-coupling product at the C-1 position of the parent pyrylium salt (**1Ba**) in *ca*. 10% yield as the sole characterized product; the normal coupling products were not obtained. It is already well known[28] that the treatment of telluraxanthylium salts with reducing agents (*e.g.*, zinc powder) or nucleophiles (*e.g.*, ammonium chloride) gives the telluraxanthyl ditellurides, produced *via* a free radical mechanism. This result evidently supports the present formation of the dimer (**3B**) proceeding *via* a similar radical mechanism. **3B** were also obtained by the reaction of **1B** with zinc powder or catalytic hydrogenation as already described.

Next, we planned the preparation of the 1,3-disubstituted 2-benzoselenopyrylium salts by the reaction of the obtained products with triphenylcarbenium tetrafluoroborate (Ph_3C^+ BF_4^-). The treatment of the 1,3-disubstituted isochromenes (**10—13**) with a small excess of Ph_3C^+ BF_4^+ in $MeNO_2$ resulted in the dehydrogenation to afford the corresponding

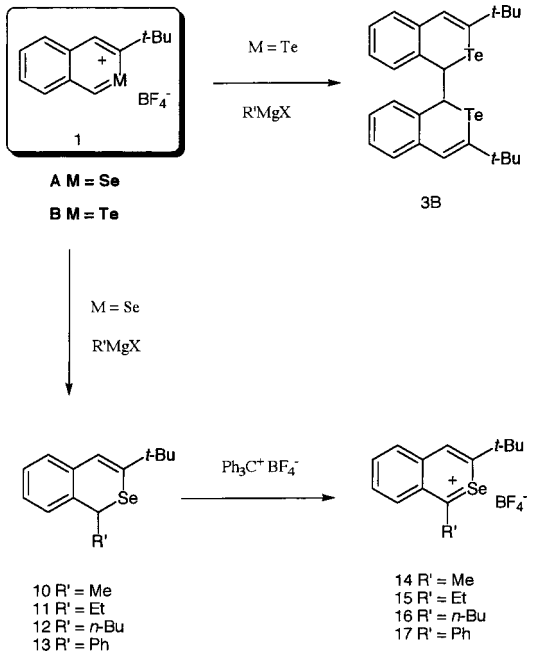

Chart 2

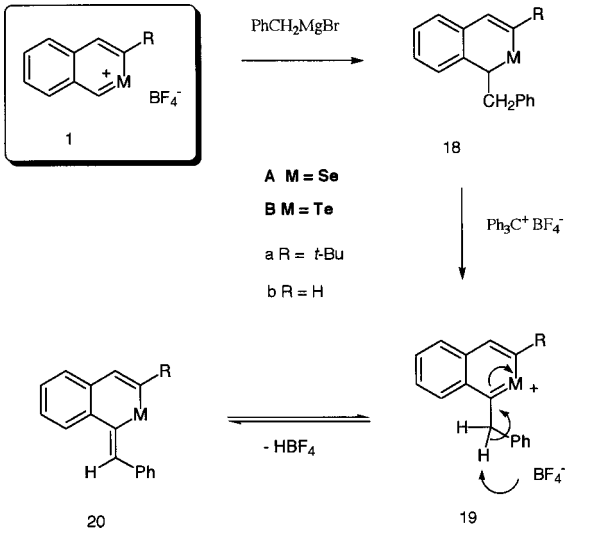

Chart 3

stable 2-benzoselenopyrylium tetafluoroborates (**14**—**17**) as yellow or green prisms in good to high yields. The unsubstituted[29] and 3-substituted 2-benzoselenopyrylium salts[16] have been prepared before, while these selenopyrylium salts (**14**—**17**) having two carbon functional groups at the C-1 and C-3 positions are hitherto unknown compounds.

Reaction of Pyrylium Salts with Benzylmagnesium Bromide The 2-benzoselenopyrylium salts (**1A**) also reacted with benzylmagnesium bromide to afford the 1-benzyl-1*H*-isoselenochromenes (**18A**), as normal coupling products in *ca.* 60% yields. It has already been found[11] that the 4-benzyl-4*H*-tellurochromenes are produced from the 2-substituted 1-benzotelluropyrylium salts using benzylmagnesium bromide as a Grignard reagent without forming dimeric-type compounds. This finding on the reaction of the pyrylium salts containing a selenium or tellurium atom with benzylmagnesium bromide suggests that the 1-benzyl-1*H*-isotellurochromenes could be obtained from the 2-benzotelluropyrylium salts (**1B**). Both the *tert*-butyl-1-benzotelluropyrylium salt (**1Ba**) and the unsubstituted telluropyrylium salt (**1Bb**) were coupled with benzylmagnesium bromide to give the desired 1-benzyl derivatives (**18Ba**, **18Bb**) as the sole product in 48 and 11% yields, respectively. The reaction of the 1-benzylisochromenes (**18A**, **18B**) with Ph_3C^+ BF_4^- afforded the desired 1-benzyl-2-benzopyrylium salts (**19**) as stable yellow prisms in *ca.* 60% yields except for the 3-unsubstituted 2-benzotelluropyrylium salts (**19Bb**), which were perhaps thermally unstable. Surprisingly, the ^{1}H-NMR spectrum of the crude isolated 1-benzyl-3-*tert*-butyl-selenopyrylium salt (**19Aa**) in CD_3CN appeared as two *tert*-butyl signals at δ 1.59 and 1.25 in a ratio of 4 : 3. This result indicates the presence of the salt (**19Aa**) and benzylidene compound (**20Aa**). Actually, the treatment of the salt (**19Aa**) by base or alumina column chromatography eluted with methylene chloride afforded (*Z*)-1-benzylidene-3-*tert*-butylisoselenochromene (**20Aa**)[17] in almost quantitative yield. For the 1-benzyltelluropyrylium salt (**19Ba**), two *tert*-butyl signals (δ 1.59 and 1.29) were observed in the ratio of 2 : 3 indicating the presence of the salt (**19Ba**) and the benzylidene derivative (**20Bb**).[17] The ratio of the unsubstituted selenopyrylium salt (**19Ab**) and the benzylidene compound (**20Ab**) was similar at *ca.* 1 : 1 in the NMR spectrum.

The fact, that **20** could be isolated clearly indicated that BF_4^-, the counter anion of the salts (**19**), abstracted the β-hydrogen of the methylene carbon of the benzyl group at the C-1 on the pyrylium cation ring (**19**) to form the olefin. In the case of the 2-benzoselenopyrylium salts (**14**—**16**) having an alkyl group at the C-1 position except a benzyl group, the β-hydrogen elimination did not occur forming any 1-methylideneisoselenochromenes.

Conclusion

In the present study, the reactivity of the 2-benzoseleno- and 2-benzotelluro-pyrylium salts towards several nucleophiles including the reducing and Grignard reagents was examined, the latter pyrylium cation is a novel heterocyclic ring system. Various 1-functionalized isoselenochromenes and isotellurochoromenes were obtained as a result, and then transformed into several 2-benzoselenopyrylium salts and 2-benzotelluropyrylium salts having two carbon functional groups at the C-1 and C-3 positions. It has become certain by the isolation of the benzylidene compounds that the β-hydrogen of the methylene carbon of the pyrylium cation ring was eliminated by BF_4^-, the counter anion of the salt. Further reactions and applications of the 2-benzopyrylium salts containing a selenium or tellurium atom are now under investigation.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 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.

$LiAlH_4$ Reduction of Pyrylium Salts (1) $LiAlH_4$ (16 mg, 0.33 mmol) was added in a small portion to a suspended mixture of **1** (0.3 mmol) in Et_2O (6 ml) at 0 °C under an argon atmosphere. The reaction mixture was stirred

at room temperature for 30 min, and then quenched by the addition of satulated aqueous Na_2CO_3 solution (5 drops). The resulting solution was dried ($MgSO_4$) and evaporated *in vacuo*. The resulting residue was chromatographed on silica gel eluted with *n*-hexane to give the isochromene (**2**). The products were identical with authentic samples.[16)]

3-*tert*-Butyl-1*H*-isoselenochromene (2Aa): Yield 59%.

1*H*-Isoselenochromene (2Ab): Yield 59%.

3-*tert*-Butyl-1*H*-isotellurochromene (2Ba): Yield 58%.

1*H*-Isotellurochromene (2Bb): Yield 56%.

DIBAL-H Reduction of Pyrylium Salts (1) DIBAL-H hexane solution (0.95 mol/l, 1.58 ml, 1.5 mmol) was added dropwise with stirring to a solution of the pyrylium salt (**1**) (1 mmol) in dry THF (20 ml) under an argon atmosphere at −20 °C. The mixture was stirred for 1 h, diluted with water (20 ml), and then extracted with CH_2Cl_2 (30 ml×3). The organic layers were washed with 5% HCl (30 ml×2) and saturated aqueous $NaHCO_3$ (30 ml×2), dried ($MgSO_4$) and evaporated *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane as eluent to give **2**.

2Aa: Yield 98%.

2Ab: Yield 92%.

2Ba: Yield 92%.

2Bb: Yield 89%.

Reaction of Pyrylium Salts (1) with Zn Dust Zn dust (80 mg) was added to a stirred solution of the pyrylium salt (**1**) (1 mmol) in dry MeCN (5 ml) under an argon atmosphere at 0 °C for 3 h. After removal of Zn dust, the mixture was evaporated *in vacuo*. The resulting residue was chromatographed on silica gel, with *n*-hexane–CH_2Cl_2 (5 : 1) as eluent to give **3**.

1,1′-Bis(*tert*-butylisoselenochromenyl) (3Aa): Yield 18%, pale yellow prisms (acetone–*n*-hexane), mp 271—273 °C. MS *m*/*z*: 502 (M^+, 2), 500 (2), 251 (100), 249 (50). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.33 (18H, s, *t*-Bu×2), 3.91 (2H, s, 1- and 1′-H), 6.88 (2H, s, 4- and 4′-H), 7.2—7.3 (8H, m, Ph-H×2). HR-MS *m*/*z* M^+ Calcd for $C_{26}H_{30}Se_2$: 502.0683. Found: 502.0691.

1,1′-Bis(*tert*-butylisotellurochromenyl) (3Ba): Yield 15%, yellow prisms (acetone–*n*-hexane), mp 235—236 °C. MS *m*/*z*: 602 (M^+, 5), 600 (10), 598 (12), 596 (8), 301 (100), 299 (90), 297 (60). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.33 (18H, s, *t*-Bu×2), 3.97 (2H, s, 1- and 1′-H), 6.88 (2H, s, 4- and 4′-H), 7.1—7.3 (8H, m, Ph-H×2). HR-MS *m*/*z* M^+ Calcd for $C_{26}H_{30}Te_2$: 602.0476. Found: 602.0472.

Hydrogenation of Pyrylium Salts (1) with Pd–C A solution of **1** (1 mmol) in dry THF (40 ml) was hydrogenated with 5% Pd–C (50 mg) with stirring under atmospheric pressure of H_2 at room temperature. The reaction mixture subjected to filtration and the filtrate was evaporated *in vacuo*. The resulting residue was chromatographed on silica gel, with *n*-hexane–CH_2Cl_2 (5 : 1) as eluent to give **3**.

3Aa: Yield 26%.

3Ba: Yield 20%.

Treatment of Pyrylium Salts (1) with NaOMe in MeOH NaOMe (28% solution in MeOH, 1 ml) was added to a solution of the pyrylium salt (**1**) (0.5 mmol) in MeOH (10 ml) under an argon atmosphere. The resulting solution was stirred for 30 min and extracted with CH_2Cl_2 (20 ml×3). The organic layers were washed with brine (30 ml×2), dried ($MgSO_4$), and evaporated *in vacuo* to give the 1-methoxy-1*H*-isochromene (**4**). Products were obtained in a nearly pure form, and decomposed during the attempted purification by silica gel chromatography. Crystalline products were recrystallized from *n*-hexane.

Treatment of Selenopyrylium Salts (1) with NaO*i*-Pr in *i*-PrOH NaO*i*-Pr (30% solution in *i*-PrOH, prepared from Na and *i*-PrOH, 1 ml) was added to a solution of the pyrylium salt (**1**) (0.5 mmol) in *i*-PrOH (10 ml) under an argon atmosphere. The resulting reaction mixture was worked up as described for the preparation of **4** to give the 1-isopropoxy-1*H*-isochromene (**5**).

Treatment of Selenopyrylium Salts (1A) with KO*t*-Bu in *t*-BuOH KO*t*-Bu (200 mg) was added to a solution of the selenopyrylium salt (**1A**) (0.5 mmol) in *t*-BuOH (10 ml) under an argon atmosphere. The resulting reaction mixture was worked up as described for the preparation of **4** to give the 1-*tert*-butoxy-1*H*-isoselenochromene (**6A**).

Treatment of Pyrylium Salts (1) with Diethylamine Diethylamine (0.6 ml) was added slowly to a suspended mixture of **1** (0.3 mmol) in benzene (6 ml) at room temperature under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min, and then extracted with benzene (20 ml×3). Benzene layer was washed with brine (30 ml×2) and dried ($MgSO_4$), and evaporated *in vacuo* to give the 1-diethylamino-1*H*-isochromene (**7**). All products (**7**) were obtained in nearly pure states. Thus, crystalline products were recrystallized from *n*-hexane.

Treatment of Selenopyrylium Salts (1A) with *n*-Butylthylamine The selenopyrylium salt (**1A**) was treated with *n*-butylamine instead of diethylamine and worked up as described for the preparation of **7** to give **8**.

1-*n*-Butyl-3-*tert*-butyl-1*H*-isoselenochromene (8Aa): IR (neat) cm^{-1}: 3340 (NH).

1-*n*-Butyl-1*H*-isoselenochromene (8Ab): IR (neat) cm^{-1}: 3340 (NH).

Treatment of Pyrylium Salts (1) with Acetone The pyrylium salt (**1**) (0.3 mmol) was disolved in dry acetone (6 ml) at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min, and then extracted with CH_2Cl_2 (20 ml×3). The organic layers were washed with brine (30 ml×2) and dried ($MgSO_4$) and evaporated *in vacuo*. The resulting residue was chromatographed on silica gel eluted with *n*-hexane–CH_2Cl_2 (1 : 1) to give **9** as a pale yellow or yellow oil.

1-Acetonyl-3-*tert*-butyl-1*H*-isoselenochromene (9Aa): IR (neat) cm^{-1}: 1722 (C=O).

1-Acetonyl-1*H*-isoselenochromene (9Ab): IR (neat) cm^{-1}: 1716 (C=O).

1-Acetonyl-3-*tert*-butyl-1*H*-isotellurochromene (9Ba): IR (neat) cm^{-1}: 1718 (C=O).

Reaction of 2-Benzoselenopyrylium Salts 1A with Grignard Reagent. 3-*tert*-Butyl-1-methyl-1*H*-isoselenochromene (10) MeMgI (4 mmol) in ether solution (4 ml) was slowly added to a suspended mixture of the pyrylium salt (**1Aa**) (3 mmol) in ether (20 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred under the conditions for 30 min, and quenched by the addition of saturated aqueous NH_4Cl solution (10 ml). The resulting mixture was extracted with Et_2O (30 ml×3). The organic layers were washed with brine (30 ml×2) and dried ($MgSO_4$) and evaporated *in vacuo*. The resulting residue was chromatographed on silica gel eluted with *n*-hexane–CH_2Cl_2 (20 : 1) to give **10** (76%), pale yellow oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.28 (9H, s, *t*-Bu), 1.60 (3H, d, *J*=7 Hz, 1-Me), 4.02 (1H, q, *J*=7 Hz, 1-H), 6.72 (1H, s, 4-H), 7.1—7.3 (4H, m, Ph-H). HR-MS *m*/*z* M^+ Calcd for $C_{14}H_{18}Se$: 266.0574. Found: 266.0576.

3-*tert*-Butyl-1-ethyl-1*H*-isoselenochromene (11) The pyrylium salt (**1Aa**) was treated with EtMgBr instead of MeMgI and worked up as described for the preparation of **10** to give **11** (69%), colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.89 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 1.28 (9H, s, *t*-Bu), 1.78 (dq, *J*=7, 7 Hz, $C\underline{H}_2CH_3$), 3.68 (1H, t, *J*=7 Hz, 1-H), 6.69 (1H, s, 4-H), 7.1—7.2 (4H, m, Ph-H). HR-MS *m*/*z* M^+ Calcd for $C_{15}H_{20}Se$: 280.0731. Found: 280.0724.

1-*n*-Butyl-3-*tert*-butyl-1*H*-isoselenochromene (12) The pyrylium salt **1Aa** was treated with *n*-BuMgCl instead of MeMgI and worked up as described for the preparation of **10** to give **12** (71%), pale yellow oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.85 (3H, t, *J*=7 Hz, $CH_2CH_2CH_2C\underline{H}_3$), 1.1—1.4 (4H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.27 (9H, s, *t*-Bu), 1.6—1.8 (2H, m, $C\underline{H}_2CH_2CH_2CH_3$), 3.75 (1H, t, *J*=7 Hz, 1-H), 6.70 (1H, s, 4-H), 7.1—7.2 (4H, m, Ph-H). HR-MS *m*/*z* M^+ Calcd for $C_{17}H_{24}Se$: 308.1044. Found: 308.1043.

3-*tert*-Butyl-1-phenyl-1*H*-isoselenochromene (13) The pyrylium salt (**1Aa**) was treated with PhMgBr instead of MeMgI and worked up as described for the preparation of **10** to give **13** (74%), yellow prisms (*n*-hexane), mp 43—44 °C. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.16 (9H, s, *t*-Bu), 5.24 (1H, s, 1-H), 6.78 (1H, s, 4-H), 6.9—7.2 (9H, m, Ph-H). HR-MS *m*/*z* M^+ Calcd for $C_{19}H_{20}Se$: 328.0731. Found: 328.0732.

1,1′-Bis(*tert*-butylisotellurochromenyl) (3B) This compound was obtained in *ca.* 10% yield by the reaction of **1B** with the Grignarn reagents (*e.g.*, MeMgI, EtMgBr, *n*-BuMgCl, PhMgBr).

Treatment of Isochromenes (10—13) with Ph_3C^+ BF_4^-: Formation of 2-Benzoselelopyrylium Tetrafluoroborate (14—17) $Ph_3C^+BF_4^-$ (187 mg, 0.55 mmol) was added to a stirred solution of the isoselenochromene (**10**) (0.5 mmol) in dry $MeNO_2$ (2 ml) and the mixture was stirred at room temperature for 2 h. To the reaction mixture was added dry Et_2O (25 ml) to precipitate the pyrylium salts.

3-*tert*-Butyl-1-methyl-2-benzoselelopyrylium Tetrafluoroborate (14): Yield 86%, pale yellow prisms ($CHCl_3$), mp 200—202 °C (decomp.). IR (KBr) cm^{-1} 1062 (BF_4^-). ^{1}H-NMR (90 MHz, CD_3CN) δ: 1.67 (9H, s, *t*-Bu), 3.53 (3H, s, 1-Me), 8.3—8.7 (4H, m, Ph-H), 8.88 (1H, s, 4-H). *Anal.* Calcd for $C_{14}H_{17}BF_4Se$: C, 47.90; H, 4.88. Found: C, 47.89, H, 4.85.

3-*tert*-Butyl-1-ethyl-2-benzoselelopyrylium Tetrafluoroborate (15): Yield 74%, yellow prisms ($CHCl_3$), mp 146—148 °C (decomp.). IR (KBr) cm^{-1} 1060 (BF_4^-). ^{1}H-NMR (90 MHz, CD_3CN) δ: 1.67 (9H, s, *t*-Bu), 1.70 (3H, t, *J*=8 Hz, $CH_2C\underline{H}_3$), 4.01 (2H, q, *J*=8 Hz, $C\underline{H}_2CH_3$), 8.1—8.5 (4H, m, Ph-H), 8.86 (1H, s, 4-H). *Anal.* Calcd for $C_{15}H_{19}BF_4Se$: C, 49.35; H, 5.25. Found: C, 49.28; H, 5.20.

1-*n*-Butyl-3-*tert*-butyl-2-benzoselelopyrylium Tetrafluoroborate (16): Yield 72%, yellow prisms ($CHCl_3$), mp 100—102 °C (decomp.). IR (KBr) cm^{-1} 1055 (BF_4^-). ^{1}H-NMR (90 MHz, CD_3CN) δ: 1.67 (9H, s, *t*-Bu), 1.13 (3H, t, *J*=7 Hz, $CH_2CH_2CH_2C\underline{H}_3$), 1.4—1.8 (4H, m,, $CH_2C\underline{H}_2C\underline{H}_2CH_3$),

3.99 (2H, t, J=8 Hz, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 8.4—8.8 (4H, m, Ph-H), 8.87 (1H, s, 4-H). *Anal.* Calcd for $C_{17}H_{23}BF_4Se$: C, 51.94; H, 5.90. Found: C, 51.84; H, 6.00.

3-*tert*-Butyl-1-phenyl-2-benzoselelopyrylium Tetrafluoroborate (**17**): Yield 77%, yellow prisms ($CHCl_3$), mp 70—72 °C (decomp.). IR (KBr) cm^{-1} 1057 (BF_4^-). ^{1}H-NMR (90 MHz, CD_3CN) δ: 1.71 (9H, s, *t*-Bu), 7.8 (5H, br s, 1-Ph), 8.0—8.5 (4H, m, Ph-H), 9.01 (1H, s, 4-H). *Anal.* Calcd for $C_{19}H_{19}BF_4Se$: C, 55.24; H, 4.64. Found: C, 55.24; H, 4.86.

Reaction of Pyrylium Salts (1) with PhCH$_2$MgBr The pyrylium salt (**1**) was treated with PhCH$_2$MgBr instead of MeMgI and worked up as described for the preparation of **13** to give **18**.

1-Benzyl-3-*tert*-butyl-1*H*-isoselenochromene (**18Aa**): Yield 59%, yellow prisms (*n*-hexane), mp 52—53 °C. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.32 (9H, s, *t*-Bu), 3.05 (2H, d, J=8 Hz, CH_2Ph), 3.99 (1H, t, J=8 Hz, 1-H), 6.80 (1H, s, 4-H), 6.9—7.3 (9H, m, Ph-H). HR-MS m/z M$^+$ Calcd for $C_{22}H_{22}Se$: 342.0888. Found: 342.0888.

1-Benzyl-1*H*-isoselenochromene (**18Ab**): Yield 31%, pale yellow prisms (*n*-hexane), mp 49—52 °C. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 3.12 (2H, d, J=8 Hz, C$\underline{H}_2$Ph), 3.95 (1H, dd, J=8, 1 Hz, 1-H), 6.74 (1H, dd, J=10, 1 Hz, 3-H), 7.04 (1H, d, J=10 Hz, 4-H), 6.8—7.3 (9H, m, Ph-H). HR-MS m/z M$^+$ Calcd for $C_{16}H_{14}Se$: 286.0261. Found: 286.0258.

1-Benzyl-3-*tert*-butyl-1*H*-isotellurochromene (**18Ba**): Yield 48%, yellow oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.31 (9H, s, *t*-Bu), 3.21 (2H, d, J=7 Hz, CH_2Ph), 3.96 (1H, t, J=7 Hz, 1-H), 6.78 (1H, s, 4-H), 6.9—7.3 (9H, m, Ph-H). HR-MS m/z M$^+$ Calcd for $C_{20}H_{22}Te$: 392.0785. Found: 392.0781.

1-Benzyl-1*H*-isotellurochromene (**18Bb**): Yield 11%, yellow oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 3.28 (2H, d, J=7 Hz, C$\underline{H}_2$Ph), 3.95 (1H, t, J=7 Hz, 1-H), 6.8—7.4 (11H, m, 3-, 4- and Ph-H). HR-MS m/z M$^+$ Calcd for $C_{16}H_{14}Te$: 336.0159. Found: 336.0151.

Treatment of Isochromenes (18) with Ph_3C^+ BF_4^-: Formation of 1-Benzyl-2-benzopyrylium Tetrafluoroborate (19) The isoselenochromene (**18**) was treated with Ph_3C^+ BF_4^- and worked up as described for the preparation of **1**4 to give **19**.

1-Benzyl-3-*tert*-butyl-2-benzoselelopyrylium Tetrafluoroborate (**19Aa**): Yield 61%, yellow prisms ($CHCl_3$), mp 120—123 °C (decomp.). IR (KBr) cm^{-1} 1064 (BF_4^-). ^{1}H-NMR (90 MHz, CD_3CN) δ: 1.59 (9H, s, *t*-Bu), 5.25 (2H, s, C$\underline{H}_2$Ph), 7.3—7.5 (9H, m, Ph-H), 8.86 (1H, s, 4-H). *Anal.* Calcd for $C_{20}H_{21}BF_4Se$: C, 56.24; H, 4.96. Found: C, 56.22; H, 4.88.

1-Benzyl-2-benzoselelopyrylium Tetrafluoroborate (**19Ab**): Yield 60%, yellow prisms ($CHCl_3$), mp 106—108 °C (decomp.). IR (KBr) cm^{-1} 1056 (BF_4^-). ^{1}H-NMR (90 MHz, CD_3CN) δ: 5.25 (2H, s, C$\underline{H}_2$Ph), 7.3—7.5 (9H, m, Ph-H), 8.96 (1H, d, J=9 Hz, 4-H), 9.57 (1H, d, J=9 Hz, 3-H). *Anal.* Calcd for $C_{16}H_{13}BF_4Se$: C, 51.79; H, 3.53. Found: C, 51.57; H, 3.43.

1-Benzyl-3-*tert*-butyl-2-benzotelluropyrylium Tetrafluoroborate (**19Ba**): Yield 60%, pale green prisms ($CHCl_3$), mp 106—108 °C (decomp.). IR (KBr) cm^{-1} 1052 (BF_4^-). ^{1}H-NMR (90 MHz, CD_3CN) δ: 1.55 (9H, s, *t*-Bu), 4.82 (2H, s, C$\underline{H}_2$Ph), 7.2—7.6 (9H, m, Ph-H), 8.92 (1H, s, 4-H). *Anal.* Calcd for $C_{20}H_{21}BF_4Te$: C, 50.49; H, 4.45. Found: C, 50.64; H, 4.47.

Treatment of 1-Benzylpyrylium Salts (19) with Basic Alumina A solution of **19** (*ca.* 0.1 mmol) in MeCN–$CHCl_3$ (1 : 5) was passed through a basic alumina column. The eluent was evaporated *in vacuo* and residue was recrystallized from *n*-hexane to give **20** quantitatively.

(*Z*)-1-Benzylidene-3-*tert*-butyisoselenochromene (**20Aa**): Yellow prisms (acetone–*n*-hexane), mp 118—120 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.28 (9H, s, *t*-Bu), 6.74 (1H, s, 4-H), 7.15—7.54 (9H, m, Ph-H), 7.41 (1H, s, 1′-H). HR-MS m/z M$^+$ Calcd for $C_{20}H_{20}Se$: 340.0731. Found: 340.0734.

(Z)-1-Benzylideneisoselenochromene (**20Ab**): Yellow prisms (acetone–*n*-hexane), mp 119—121 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.79 (1H, br d, J=9.9 Hz, 3-H), 7.02 (1H, d, J=9.9 Hz, 4-H), 7.15—7.52 (9H, m, Ph-H), 7.40 (1H, s, 1′-H). HR-MS m/z M$^+$ Calcd for $C_{16}H_{12}Se$: 284.0105. Found: 284.0103.

(*Z*)-1-Benzylidene-3-*tert*-butyisotellurochromene (**20Ba**): Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.24 (9H, s, *t*-Bu), 6.86 (1H, s, 4-H), 7.18—7.44 (8H, m, Ph-H), 7.48 (1H, s, 1′-H), 7.53 (1H, br d, J=7.8 Hz, 8-H). HR-MS m/z M$^+$ Calcd for $C_{20}H_{20}Te$: 390.0628. Found: 390.0627.

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