1-Benzoselenopyrylium Salts and 1-Benzotelluropyrylium Salts: Preparations, Structures and Reactions

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Abstract: This review is segmented into three main parts; the preparations, structures and reactions of the 1-benzoselenopyrylium and 1-benzotelluropyryrlium salts. Synthetic work has been achieved by transformation from the selenochromones and tellurochromones in two steps. A study shows that these salts, although being stable compounds, are highly reactive with various nucleophiles to afford the successful 2- or 4-substituted selenochromene and tellurochromene derivatives.

Keywords: 1-benzoselenopyrylium salt, 1-benzotelluropyrylium salt, selenochromone, tellurochromone, 4*H*-selenochromene, 4*H*-tellurochromene.

1. INTRODUCTION

In recent years, the chemistry of the selenopyrylium [1] and telluropyrylium salts [1, 2], six-membered heterocyclic cations containing a selenium or tellurium element, has attracted much attention when compared to the thiopyrylium salts [1]. Monocyclic **I** [3], benzene ring-fused **II** [3b, 4], **III** [5] and dibenzo derivatives **IV** [6] were prepared and their reactivities were also briefly examined. With regard to the 1-benzoselenopyrylium **IIA** and 1-benzotelluropyrylium salts **IIB**, the preparation of the parent selenopyrylium salt **IIA-1** was reported by Degani and co-workers [7] in 1964, while Renson and co-workers [8] described the synthesis of the 2-phenyl- and 4-phenyl-selenopyrylium salts, which were converted into the 2,4-diphenyl derivative. These four derivatives of the selenopyrylium salts were isolated as perchlorates. The telluropyryluim skeleton **IIB-1** was also synthesized as a perchlorate from the corresponding chromene by Sadekov and co-workers [4a] in 1986. Detty and co-workers reported the preparation [3b] of the several derivatives **IIB-2** having a methoxy group on the benzene ring and described the condensation reactions [3a, c] of a 2-alkyl or 4-alkyl-substituted telluropyrylium salt with a carbonyl containing compound. However, the reactivities of the simple ring system of the 1-benzoselenopyryrlium **IIA** and 1-benzotelluropyrylium salts **IIB**, in particular toward nucleophiles have only been briefly examined. The reason for this is as follows. In Detty's synthetic method for the preparation of the tellurochromones, precursors for the preparation of the telluropyrylium salts **IIB-2** require the Friedel-Crafts reaction of β-(aryltelluro)cinnamoyl chlorides **V** [4b]. The requisite chromones can not be obtained in the absence of a strong electron-donating group such as OMe at the C-7 and (or) C-5 positions on the benzene ring. In this review, an outline of our recent results of the 1-benzoselenopyrylium and 1-benzotelluropyrylium salts (preparations, structures and reactions) will be presented. The X-ray data for these pyrylium salts are also newly reported.

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2. PREPARATION

2-1. 1-Benzoselenopyrylium and 1-Benzotelluropyrylium Salts

The synthesis of the 1-benzoselenopyryrlium **17** [9] and 1-benzotelluropyrylium salts **18** [10] from the corresponding chromones **5, 6**, [11] which were simply prepared by the reaction of the *o*-bromophenyl ethynyl ketones **2** with sodium hydrogen selenide (NaHSe) or telluride (NaHTe) [12] is shown in Scheme **1**. The synthetic method for the preparation of the selenochromones **5** and tellurochromones **6** is based on the intramolecular ring closure of a -SeH or -TeH moiety into a triple bond; this methodology was described in previous reviews [13, 14].

The starting materials, *o*-bromophenyl ethynyl ketones **2**, were readily prepared from *o*-bromobenzoyl chloride **1** by the Sonogashira reaction [15]. The benzoyl chloride **1** was coupled with various 1-substituted acetylenes in the presence of a catalytic amount of bis(triphenylphosphine)dichloro-palladium(II) and copper (I) iodide to give the corresponding **2** in good yields. For the trimethylsilyl (TMS) derivatives, this cross-coupling reaction did not proceed and only the homo-coupling product of the trimethylsilylacetylene was obtained. Therefore, the benzylchlorobis(triphenylphosphine) palladium(II)-induced coupling reaction of the benzoyl chloride with organotin reagents reported by Stille and co-workers [16] was applied. This palladium-catalyzed coupling reaction of **1** with [(trimethylsilyl)ethynyl]tributylstannane [17] afforded the desired compound **2A**. For the preparation of the selenochromones **5** and tellurochromones **6**, we first examined the conversion to the phenylchalcogenols **3**, **4** from the alkynyl phenyl ketones **2**. The treatment of **2** with NaHSe and NaHTe in DMF [12] resulted in a direct ring closure to afford the selenochromones **5** and tellurochromones **6**, respectively, as the sole product in moderate to good yields except for **6A**. The TMS derivative **2A** gave the 2-unsubstituted selenochromone **5** and tellurochromones **6** by removal of the TMS group under these reaction conditions. No five-membered cyclization products **7**, **8** were obtained.

In order to obtain the selenochromenes **9** and tellurochromenes **10**, the precursors for the preparation of the

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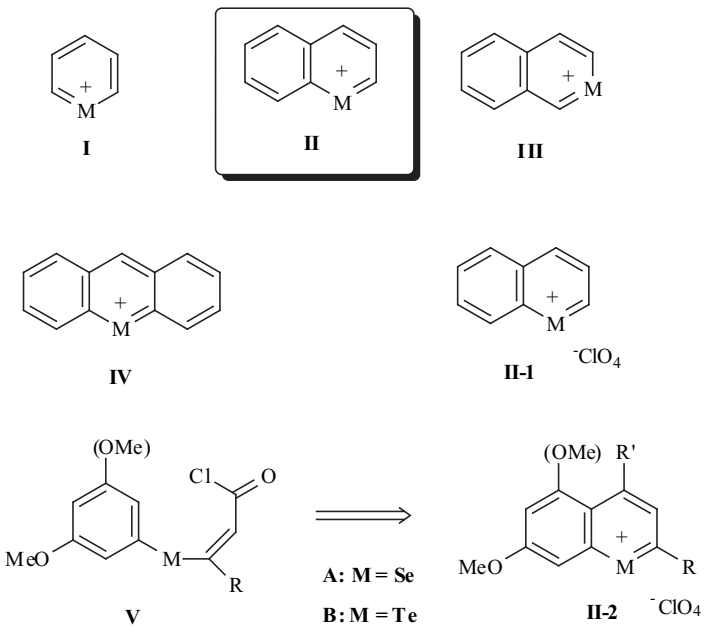
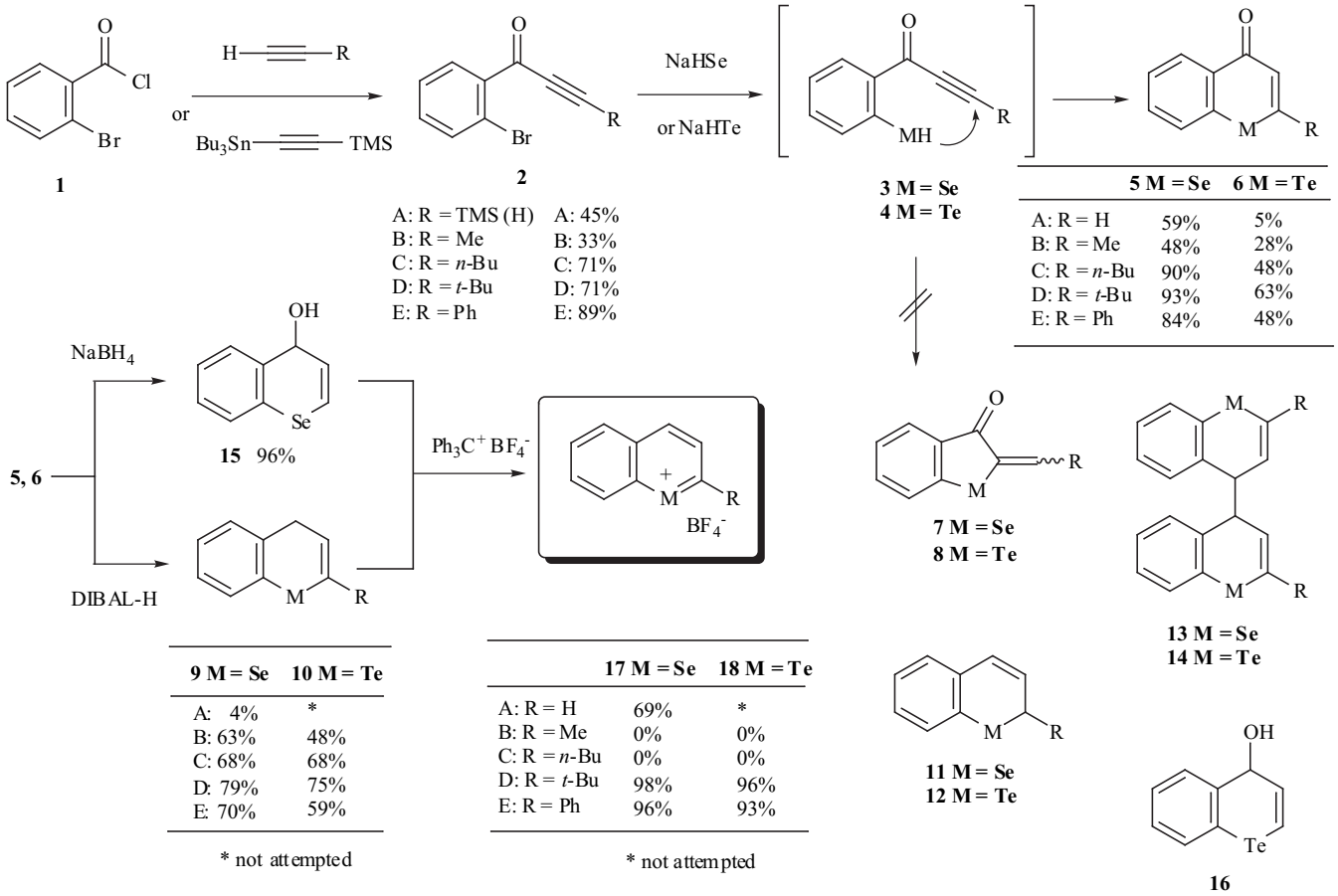


Fig. (1).

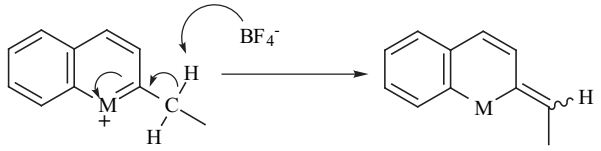


Scheme 1.

pyrylium salts **17, 18**, the diisobutylaluminium hydride (DIBAL-H) reduction [3b, 4b] was used for the conversion of the carbonyl group into the methylene. The DIBAL-H reduction of **5, 6** gave the 4*H*-selenochromenes **9** and 4*H*-tellurochromenes **10** in moderate to good yields. The 4*H*-chromenes **9, 10** were free from their regioisomers **11, 12**, while the dimeric products **14** were determined to be approximately formed in 3-8% yields in the case of the tellurochromones **6**. A similar reduction of the 2-unsubstituted selenochromone **5A** afforded **9A** in a very poor yield (*ca*. 4%

yield) together with 2*H*-selenochromene **11A**, its regioisomer, in 15% yield. Therefore, we selected 4-hydroxy-4*H*-selenochromene **15** as the precursor for the preparation of the 2-unsubstituted selenopyrylium salt **17A**. The $NaBH_4$ reduction of **5A** produced the unstable 4-hydroxy-4*H*-selenochromene **15** in almost quantitative yield. Therefore, compound **15** was used for the next step without purification. The 4-hydroxytellurochromene **16** was too unstable to isolate as it decomposed during the usual work-up. In the case of the reduction with DIBAL-H or $NaBH_4$ of the selenochromones **5**, the 2*H*-selenochromenes **11** were never obtained. Also, the dimeric products **13** could not be found after the DIBAL-H reduction of **5**, while a similar reduction of the 1-benzotellurochromones **6** gave the corresponding dimers **14**.

The treatment of the 2-*tert*-butylchromenes **9D, 10D** and 2-phenylchromenes **9E, 10E** with 1.05 equivalent of triphenylcarbenium tetrafluoroborate (Ph_3C^+ BF_4^-) in $MeNO_2$ at room temperature, followed by the addition of dry Et_2O gave the desired 1-benzoselenopyrylium **17D, 17E** and 1-benzotelluropyrylium tetrafluoroborates **18D, 18E** in almost quantitative isolated yields as stable yellow or green prisms, respectively. However, the similar treatment of the chromenes **9B, 9C** and **10B, 10C** having a primary alkyl group at the C-2 position never afforded the corresponding stable products. The 2-methyl and 2-*n*-butyl derivatives **17B, 17C, 18B, 18C** could not be isolated, although the formation of the salts could be observed in the ^1H NMR spectra. The unsubstituted selenopyrylium salt **17A** was similarly obtained by the treatment of the crude 4-hydroxy-4*H*-selenochromene **15** with Ph_3C^+ BF_4^- in acetic acid instead of $MeNO_2$ in 69% overall yield from **5A** as stable pale green prisms. This distinction between a primary alkyl group and others at the C-2 substitution for the stability of the pyrylium salts **17, 18** is definitely explained below. Tetrafluoroborate (BF_4^-), the counter anion of the salts **19, 20** eliminated the β-hydrogen of the methylene of the primary alkyl group forming the unstable *exo*-methylene compound **21, 22**. Therefore, the salts **17B, 17C** and **18B, 18C** were decomposed during the isolation operation. In our previous study [5], we determined the elimination of the β-hydrogen of the benzyl group from the 1-benzyl-2-benzotelluropyrylium salts.



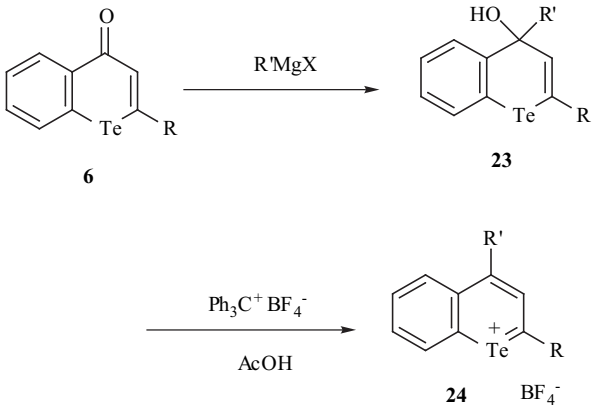
19: M = Se
20: M = Te

21: M = Se
22: M = Te

Scheme 2.

2-2. 2,4-Disubstituted 1-Benzotelluropyrylium Salts

The 1-benzotelluropyrylium salts **24** having two carbon functional groups at the C-2 and C-4 positions were prepared from the 2-substituted tellurochromones **6D**, **6E** [11] through an easy two-step route as shown in Scheme **3** [18]. The reaction of **6D**, **6E** with a small excess of methylmagnesium iodide produced the 4-hydroxy-4-methyl-4*H*-tellurochromenes **23Da**, **23Ea** in good yields. The ethyl-, phenyl- and benzylmagnesium bromides (chlorides) also smoothly reacted with the tellurochromones **6D**, **6E** to afford the corresponding coupling products **23Db-d**, **23Eb-d** in good yields. These compounds **23** were unstable and decomposed during the purification by silica gel chromatography. Thus, 4-hydroxy-4*H*-tellurochromenes **23** were used in the next step after treatment with charcoal in ethanol. Treatment of the 4-substituted 4-hydroxytellurochromenes **23** with 1.05 equivalents of Ph_3C^+ BF_4^- in acetic acid afforded the desired 1-benzotelluropyrylium tetrafluoroborates **24** by the introduction of the carbon functional group at the C-4 position in high isolated yields as yellow prisms (Scheme **3**).



6 **23** **24**

	D: R = *t*-Bu	E: R = Ph
a: R' = Me	88%	73%
b: R' = Et	80%	81%
c: R' = Ph	89%	83%
d: R' = CH_2Ph	78%	73%

Scheme 3.

The preparation of the 1-benzoselenopyrylium salts having two carbon functional groups at the C-2 and C-4 positions by the reaction of the 2-substituted 1-benzoselenopyrylium salts **17** with Grignard reagents is described in the following section.

3. X-RAY ANALYSIS

The molecular structures of 1-benzoselenopyrylium **17D** and 1-benzotelluropyrylium salt **18D**, which were uncharacterized ring systems by X-ray crystallographic analysis, were determined for the first time [19].

The single crystals of **17D** and **18D** were obtained by recrystallization from a saturated dichloromethane solution. The crystal system of both the seleno- and telluropyrylium salts was isomorphous (*orhorhmbic*, *P*nma) and the analyses revealed the perfect planarity of the ring systems, which had mirror planes through the heterocycles. Figs. (**2** and **3**) show the molecular structures of the 1-benzoselenopyrylium **17D** and 1-benzotelluropyrylium salts **18D**, respectively. The selected bond lengths and angles of **17D** and **18D** are listed in Table **1** and **2**. In the solid state, the 1-benzoselenopyrylium ring system and the tellurium derivative showed no important interaction with the counter BF_4^- anion in

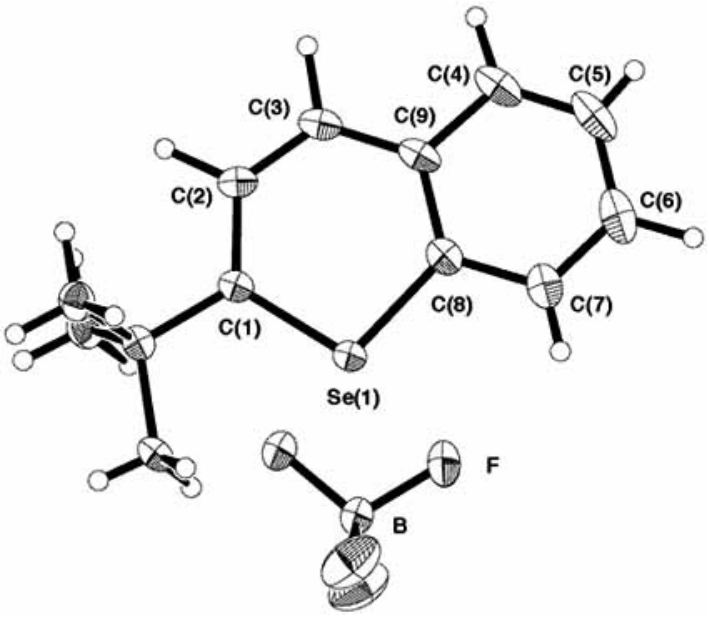


Fig. (2). ORTEP drawings of **17D** with 50% probability level.

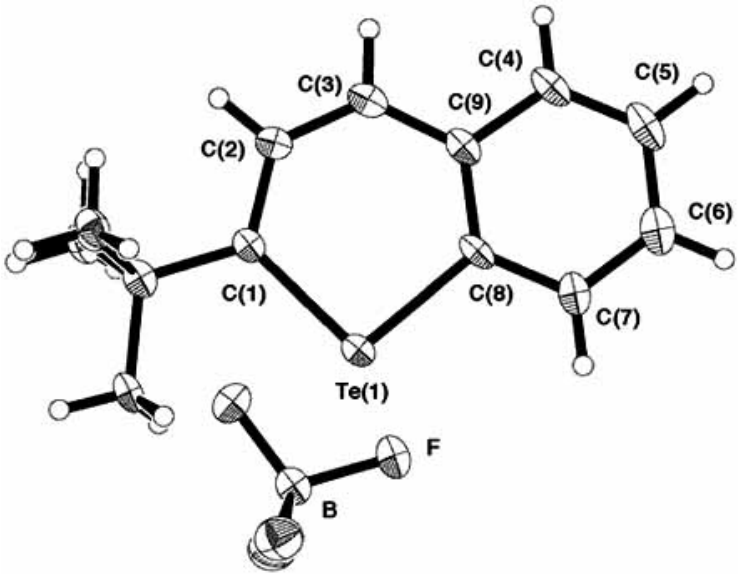


Fig. (3). ORTEP drawings of **18D** with 50% probability level.

both cases. The closest distance between fluorine in the borate and Se or Te atoms in these heterocycles are 3.378 Å (for **17D**) and 3.429 Å (for **18D**).

The selenium-carbon (1) bond lengths in **17D** (1.814 Å) is shorter than the typical Csp^2-Se bond lengths (average 1.970 Å), and were close to the C=Se double bond lengths reported in selenocarbonyl compounds (1.774 and 1.790 Å). Regarding the tellurium-carbon (1) bond length (2.010 Å) in **18D**, it is shorter than the C-Te single bond length (2.12 Å). These C-Se and C-Te bond shortenings and planarities of the heterocycles observed in **17D** and **18D** are ascribable to the π-bond conjugation in both the seleno- and telluropyrylium ring systems, although the ratio of the contributions of the resonance structures and π-delocalizations are not yet fully detailed. These bond shortenings and planarities of the ring system have also been observed in the 2-benzoseleno- and telluropyrylium salts [5b].

4. REACTIONS

The reactivities of the selenopyrylium **17** and telluropyrylium salts **18** mainly using the stable isolated 2-*tert*-butyl and 2-phenyl derivatives **D, E** were examined.

4-1. Hydride Reduction

The hydride reactions of the 1-benzoselenopyrylium **17A, D, E** and 1-benzotelluropyrylium salts **18D, E** were examined as shown in Scheme **4** [10, 20]. The $LiAlH_4$

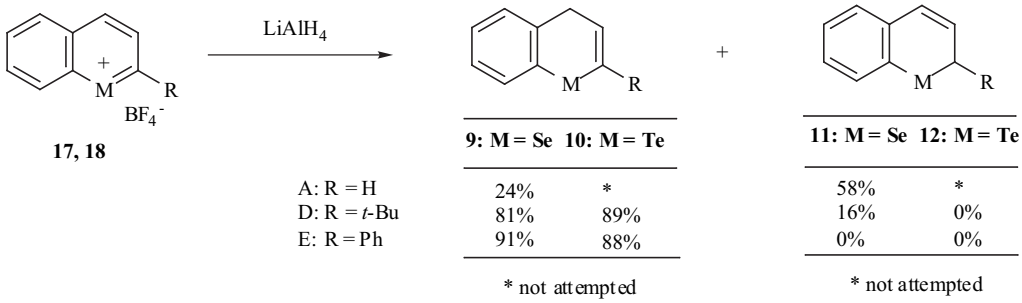
Table 1. Selected Bond Lengths (Å) and Angles (°) of 17D

Se(1)–C(1)	1.814(4)	Se(1)–C(8)	1.854(4)
C(1)–C(2)	1.396(5)	C(2)–C(3)	1.365(6)
C(3)–C(9)	1.411(6)	C(4)–C(5)	1.356(7)
C(4)–C(9)	1.415(6)	C(5)–C(6)	1.424(9)
C(6)–C(7)	1.355(8)	C(7)–C(8)	1.411(6)
C(8)–C(9)	1.422(5)		
C(1)–Se(1)-C(8)	101.4(2)	Se(1)-C(1)–C(2)	121.3(3)
C(1)–C(2)–C(3)	126.2(4)	C(2)–C(3)–C(9)	127.1(4)
C(5)–C(4–C(9)	122.1(5)	C(4)–C(5–C(6)	119.7(5)
C(5)–C(6)–C(7)	120.2(5)	C(6)–C(7)–C(8)	120.5(5)
Se(1)-C(8–C(7)	117.0(3)	Se(1)-C(8)–C(9)	122.9(3)
C(7)–C(8)–C(9)	120.1(4)	C(3)–C(9)–C(4)	121.6(4)
C(3)–C(9)–C(8)	121.1(3)	C(4)–C(9)–C(8)	117.3(5)

Table 2. Selected Bond Lengths (Å) and Angles (°) of 18D

Te(1)-C(1)	2.010(4)	Te(1)-C(8)	2.050(5)
C(1)-C(2)	1.412(7)	C(2)-C(3)	1.376(9)
C(3)-C(9)	1.406(7)	C(4)-C(5)	1.359(8)
C(4)-C(9)	1.427(6)	C(5)-C(6)	1.396(9)
C(6)-C(7)	1.395(8)	C(7)-C(8)	1.407(7)
C(8)-C(9)	1.416(7)		
C(1)-Te(1)-C(8)	96.5(2)	Te(1)-C(1)-C(2)	120.2(4)
C(1)-C(2)-C(3)	128.3(5)	C(2)-C(3)-C(9)	128.9(5)
C(5)-C(4)-C(9)	122.5(5)	C(4)-C(5)-C(6)	119.7(5)
C(5)-C(6)-C(7)	120.7(6)	C(6)-C(7)-C(8)	119.5(6)
Te(1)-C(8)-C(7)	117.0(4)	Te(1)-C(8)-C(9)	122.2(4)
C(7)-C(8)-C(9)	120.8(4)	C(3)-C(9)-C(4)	119.2(5)
C(3)-C(9)-C(8)	124.0(4)	C(4)-C(9)-C(8)	116.9(5)

reduction of the parent selenopyrylium salts **17A** in Et_2O or THF at 0°C produced a mixture of 4*H*-selenochromene **9A** and 2*H*-selenochromene **11A**, which could be separated by silica gel chromatography; the latter chromene was the major product. A similar reduction of the 2-*tert*-butylselenopyrylium salts **17D** predominantly afforded the 4*H*-selenochromene **9D** in 81% yield together with the 2*H*-derivative **11D** in 16% yield. In contrast, the 2-phenyl-



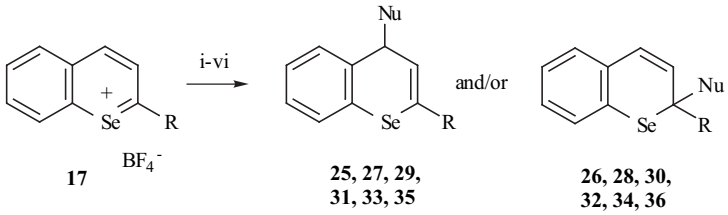
Scheme 4.

selenopyrylium salt **17E** was reduced by $LiAlH_4$ to produce the 4*H*-selenochromene **9E** in 91% yield as the sole product. The $LiAlH_4$ reduction of the telluropyrylium salts **18D, 18E** also gave the 4*H*-tellurochromenes **10D** and **10E** in 89 and 88% yields, free of the regioisomer, respectively.

4-2. Nucleophiles

It was unexpectedly found that the major products from the $NaBH_4$ reduction of the selenopyrylium salts **17** in MeOH were the 4-methoxy-4*H*-chromenes **25** and **26** and not the reduced products. This fact indicates that MeOH operated as a nucleophile toward the pyrylium salts **17**. In actuality, the addition of NaOMe to this reaction increased the yields of the products. Some reactions of the 1-benzoselenopyrylium salts **17** with nucleophiles were examined as shown in Scheme **5** [20], and these results are summarized in Table **3**. The selenopyrylium salts **17A** and **17D** reacted with *i*-PrONa in *i*-PrOH to afford 2-isopropoxy-2*H*- **28A** and 4-isopropoxy-4*H*-selenochromene **27D** in 92 and 91% yields, respectively. When the 2-phenylpyrylium salt **17E** was treated under the same conditions, it gave the corresponding product **27E** in only a 12% yield. Treatment of the 2-unsubstituted salt **17** with *t*-BuOK in *t*-BuOH resulted in the nucleophilic attack of *t*-BuO^- at the C-2 position to produce the 2-*tert*-butoxy-2*H*-chromene **30A** in 80% yield. The salts **17D** and **17E** having a *tert*-butyl or phenyl group at the C-2 position failed to afford any selenochromenes even with a high concentration of butoxide ion due to their steric hindrance.

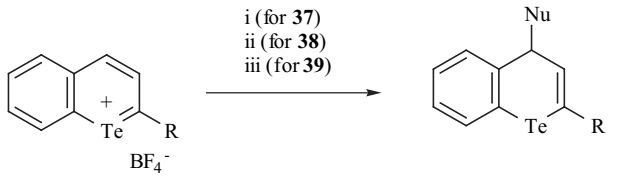
These results suggested that the selenopyrylium salts **17** may also have high reactivities toward other nucleophiles. The reaction of **17** with diethylamine in benzene at room temperature proceeded as expected. When a *tert*-butyl or phenyl group was located at the C-2 position of **17**, the corresponding 4*H*-selenochromenes **31D** and **31E** were formed in high yields. However, the 2-unsubstituted salt **17A** underwent a nucleophilic addition at the C-2 position to give **32A** in 74% yield. The reaction of **17** with a primary amine, such as *n*-butylamine, produced no characterizable products in the case of **17A**, while the chromenes **33D** and **33E** having a *tert*-butyl or phenyl group at the C-2 position could be obtained from the corresponding salts in excellent yields.



Scheme 5.
Reagents and conditions: i, NaOMe, MeOH, room temp., 30min (for **25**, **26**), ii, NaO*i*-Pr, *i*-PrOH, room temp., 30min (for **27**, **28**), iii, KO*t*-Bu, *t*-BuOH, room temp., 30min (for **29**, **30**), iv, $NHEt_2$, benzene, room temp., 30min (for **31**, **32**), v, NH_2*n*-Bu, benzene, room temp., 30min (for **33**, **34**), vi, KCN, 18-crown-6, MeCN, room temp., 30min (for **35**, **36**).

Table 3. 2- or 4-Substituted Selenochromenes 25-36

Nu		Compound Yield (%)	Compound Yield (%)
OMe	A: R = H	**25A** (0)	**26A** (93)
	D: R = *t*-Bu	**25D** (21)	**26D** (75)
	E: R = Ph	**25E** (91)	**26E** (0)
O*i*-Pr	A: R = H	**27A** (0)	**28A** (92)
	D: R = *t*-Bu	**27D** (91)	**28D** (0)
	E: R = Ph	**27E** (12)	**28E** (0)
O*t*-Bu	A: R = H	**29A** (0)	**30A** (80)
NEt_2	A: R = H	**31A** (0)	**32A** (74)
	D: R = *t*-Bu	**31D** (93)	**32D** (0)
	E: R = Ph	**31E** (96)	**32E** (0)
NH*n*-Bu	D: R = *t*-Bu	**33D** (91)	**34D** (0)
	E: R = Ph	**33E** (96)	**34E** (0)
CN	A: R = H	**35A** (0)	**36A** (9)
	D: R = *t*-Bu	**35D** (75)	**36D** (0)
	E: R = Ph	**35E** (85)	**36E** (0)



18D: R = *t*-Bu
18E: R = Ph

	D	E
37: Nu = OMe	91%	88%
38: Nu = NEt_2	89%	80%
39: Nu = CN	15%	13%

Scheme 6.
Reagents and conditions: i, NaOMe, MeOH, room temp., 30min; ii, $HNEt_2$, benzene, room temp., 30min; iii, KCN, 18-crown-6, MeCN, room temp., 30min.

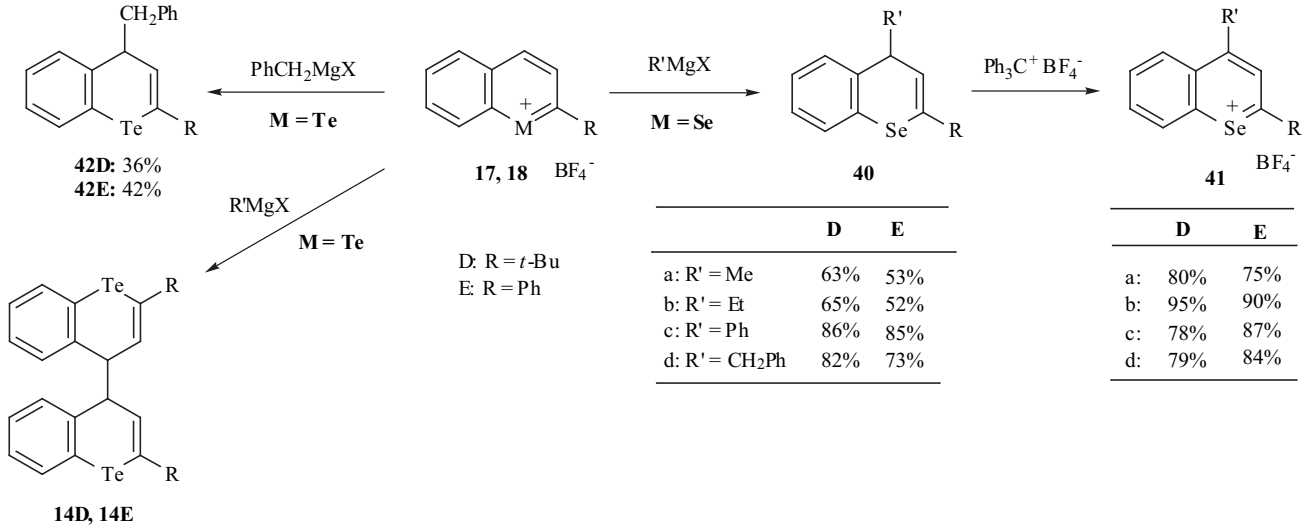
Moreover, nucleophilic attack of a cyanide ion (KCN) in the presence of 18-crown-6 as a phase transfer catalyst in MeCN to the C-4 position was found to produce the 4-cyano-4*H*-selenochromenes **35D, 35E** in good yields [20], while the yield of 2-cyano-2*H*-chromene **36A** was poor. A long reaction time decreased the yields of the products due to their instability.

The reactivities of the telluropyrylium salts **18** toward nucleophiles using the stable isolated substrates **18D** and **18E** were also examined as shown in Scheme **6** [10]. The 4-methoxy- **37** and 4-diethylamino-4*H*-tellurochromenes **38** were obtained in good yields. Secondary (e.g., isopropanol) and tertiary alcohols (e.g., *tert*-butanol) containing the corresponding alkoxide and primary amine (e.g., *n*-butylamine) never completely reacted to give any products. The reaction of **18D** and **18E** with a cyanide ion (KCN) in the presence of 18-crown-6 as a phase transfer catalyst in MeCN produced the 4-cyano-4*H*-tellurochromenes **39**, while the yields were poor due to their instability.

4-3. Grignard Reagents

To obtain more highly substituted derivatives, the Grignard reaction with the salts **17, 18** was carried out (Scheme **7**) [10, 22]. The reaction of the 2-*tert*-butyl-1-benzoselenopyrylium salts **17D** and 2-phenyl-1-benzoselenopyrylium salts **17E** with 1.2 equivalents of methylmagnesium iodide in Et_2O at 0 °C resulted in nucleophilic addition at the C-4 position to produce the 4-methyl-4*H*-selenochromenes **40Da** and **40Ea** in 63% and 53% yields, respectively. The 4-ethyl-4*H*-selenochromenes **40Db**, **40Eb**, 4-phenyl-4*H*-selenochromenes **40Dc**, **40Ec** and 4-benzyl-4*H*-selenochromenes **40Dd, 40Ed** were similarly obtained by the treatment with the corresponding Grignard reagents in good to high yields. Their regioisomers, the 4-substituted 2*H*-selenochromenes were never been produced. In contrast, the treatment of the telluropyrylium salts **18** with Grignard reagents, such as methyl-, ethyl- and phenyl-magnesium bromides (iodides) resulted in a decomposition to slightly produce the complex mixture including the dimeric products **14**. On the contrary, the use of benzylmagnesium bromide as a Grignard reagent gave the 4-benzyl-4*H*-tellurochromenes **42D**, **42E**, normal coupling products in moderate yields. In this case, no dimers **14** were formed.

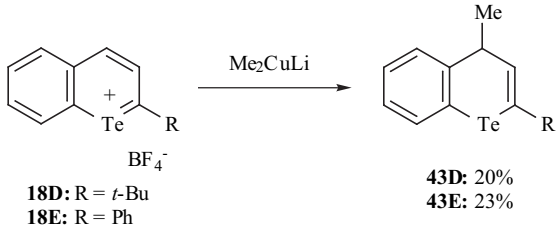
Next, in order to obtain the 1-benzoselenopyrylium salts having carbon functional groups at both the C-2 and C-4 positions, the reaction of the selenochromenes **40** with $Ph_3C^+ BF_4^-$ was carried out. The treatment of 2-*tert*-butyl-4-methylselenochromene **40Da** with 1.1 equivalents of $Ph_3C^+ BF_4^-$ in $MeNO_2$ afforded the desired 2-*tert*-butyl-4-methyl-1-benzoselenopyrylium tetrafluoroborate **41Da** in 80% yield as stable green prisms. Application of the synthesis for the



	D	E
a: R' = Me	63%	53%
b: R' = Et	65%	52%
c: R' = Ph	86%	85%
d: R' = CH_2Ph	82%	73%

	D	E
a:	80%	75%
b:	95%	90%
c:	78%	87%
d:	79%	84%

Scheme 7.



Scheme 8.

other 2,4-disubstituted 1-benzoselenopyrylium salts **41** was also successful. All salts **41Ea**, **41Db**, **41Eb, 41Dc, 41Ec, 41Dd** and **41Ed** were isolated, and proved to be quite stable and not sensitive to air and light; but readily decomposed upon contact with a protic solvent such as water and methanol.

4-4. Organocopper Reagents

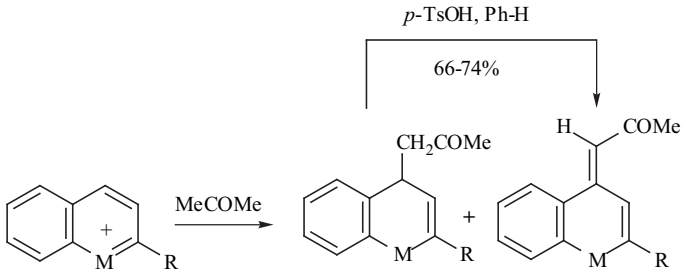
The reaction of the 1-benzotelluropyrylium salts **18** with Grignard reagents except for benzylmagnesium bromide resulted in the decomposition of the starting material to afford a complex mixture including a small quantity of the dimeric-type product **14** as shown in Scheme **7**. However, we found that the reaction of the pyrylium salt **18** with R_2CuLi [23] formed a carbon-carbon bond at the C-4 position to give the desire 4-substituted tellurochromenes **43** (Scheme **8**). The 2-*tert*-butyl-1-benzotelluropyrylium **18D** and 2-phenyl-1-benzotelluropyrylium salt **18E** reacted with 5 equivalents of Me_2CuLi, which was easily generated in situ from 2 mol of MeLi and 1 mol of CuI in Et_2O to give the 4-methyl-4*H*-tellurochromenes **43D** and **43E** in 20 and 23%, respectively, with a small amount of unknown compounds [24, 25].

4-5. Active Methylene Compounds

The salts **17** and **18** readily reacted with dry acetone even at room temperature in analogy with 2-benzotelluropyrylium salts [26] as shown in Scheme **9**. This was inspite of the absence of an electron-withdrawing group [27], which enhanced the reactivity of the pyrylium ring. 4-Acetonyl-2-*tert*-butyl-4*H*-selenochromene **44D** and (*E*)-4-acetonylidene-4*H*-selenochromene **46D** were produced yields in 19% and 23%, respectively; the former would probably be the initial product, and was easily dehydrogenated to afford **46D** by refluxing in the presence of *p*-toluenesulfonic acid (TsOH) in benzene. Similarly, **44E**, **45D**, **45E**, **46E**, **47D** and **47E** were also obtained from **17E**, **18D** and **18E** [10, 28].

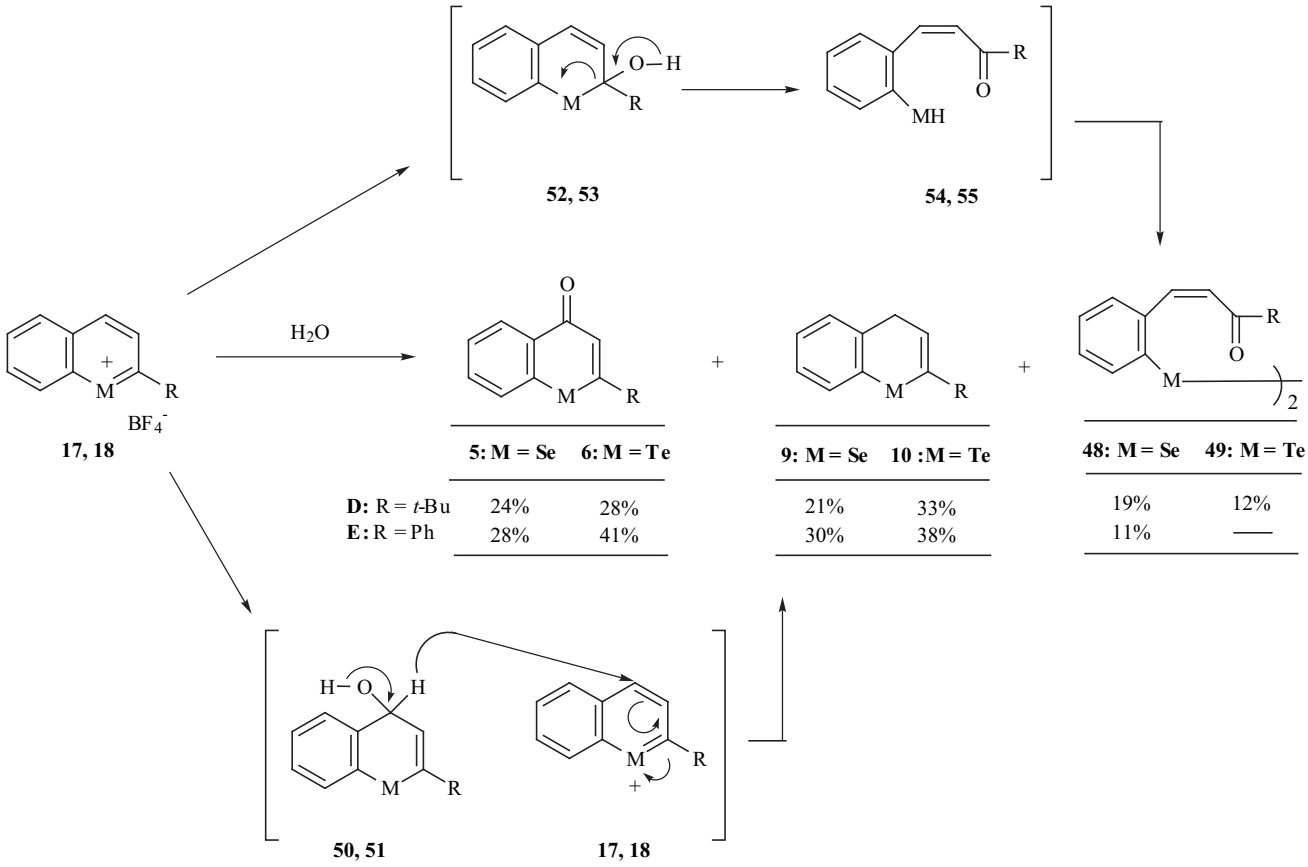
4-6. Hydrolysis

The hydrolysis of the pyrylium salts **17, 18** was next examined (Scheme **10**). The treatment of the *tert*-butyl derivative **17D** with water containing of a small amount of potassium ferricyanide yielded the diphenyl diselenide **48D**, the selenochromone **5D** and the 4*H*-selenochromene **9D** in 19, 24 and 21% yields, respectively. It is already well known that the oxidation of the phenylselenol(tellurol) with an oxidizing agent gave the diphenyl diselenide(telluride). Thus, a possible mechanism for the formation of **48, 49** is shown in Scheme **10** [10, 28]. The initial intermediate, 2-hydroxy-2-*tert*-butyl-2*H*-selenochromene **52D**, generated by the nucleophilic attack of a hydroxy group at the C-2 position of **17D**, would undergo ring opening with the migration of the hydroxyl proton to form the phenylselenol **54D**. The resulting selenol **54D** would be oxidized by air or potassium ferricyanide to give the diselenide **48D**. The formation of **5D** and **9D** might be elucidated by the process involving an intermolecular hydride shift from the 4-hydroxyselenochromene **50D** to the parent 1-benzoselenopyrylium cation **17D**, analogously with the hydrolysis of the 2-phenylthiopyrylium salt [29]. The hydrolysis of the 2-phenylselenopyrylium **17E** and 2-*tert*-butyltelluropyrylium salts **18D** also produced the corresponding dicharcogenides **48E**, **49D**, chromones **5E**, **6D** and 4*H*-chromene **9E**, **10D**, respectively. In the case of the hydrolysis of the 2-phenyltelluropyrylium salt **18E**, the chromone **6E** (41%



	44	45	46	47
	M = Se	M = Te	M = Se	M = Te
D: R = *t*-Bu	19%	19%	23%	28%
E: R = Ph	18%	20%	25%	22%

Scheme 9.



Scheme 10.

yield) and the chromene **10E** (38% yield) were obtained without producing the diphenyl ditelluride **49E**. This mechanism for the formation of **5**, **6** and **9**, **10** was supported by the fact that the compound pairs **5**, **6** and **9**, **10** were produced in approximately equal amount.

CONCLUSIONS

In this review, the synthesis of the 1-benzoselenopyrylium and 1-benzotelluropyrylium salts without an OMe group on the benzene ring was achieved. The structures (X-ray crystallographic study) and properties associated with the stabilities of these salts were elucidated. The 4*H*-selenochromenes and tellurochromenes having a functional group at the C-4 position were obtained by the reactions of the parent pyrylium salts with various nucleophiles. The 2,4-disubstituted chromenes, which were prepared by the treatment of the pyrylium salts with some Grignard reagents, were converted into the corresponding 1-benzoselenopyrylium and 1-benzotelluropyrylium salts.

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[19] Crystal data for **17D**. $C_{13}H_{15}BF_4Se$ MW = 337.03; *orthorhombic*; space group *P*nma (#62); a = 13.5160(5) Å, b = 6.8290(1) Å, c = 14.9680(5) Å, V = 1381.56(6) Å^3; Z = 4; D_{calcd} = 1.620 g/cm^3; $2\theta_{max}$ = 55°; T = 200 K; $R_1(I > 2\sigma–I)$ = 0.046; wR_2 (all data) = 0.143; *GOF* = 1.02 for 1544 reflections and 110 parameters.
Crystal data for **18D**. $C_{13}H_{15}BF_4Te$ MW = 385.67; *orthorhombic*; space group *P*nma (#62); a = 13.9670(8) Å, b = 6.8250(3) Å, c = 14.8920(9) Å, V = 1419.6(1) Å^3; Z = 4; D_{calcd} = 1.804 g/cm^3; $2\theta_{max}$ = 55°; T = 200 K; $R_1(I > 2\sigma–I)$ = 0.056; wR_2 (all data) = 0.172; *GOF* = 1.27 for 1429 reflections and 110 parameters.
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