SHORT PAPER

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A facile preparation of 1-benzoselenopyrylium salts[1†]

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The general preparation of unsubstituted and 2-substituted 1-benzoselenopyrylium salts **4** from the selenochromen-4-ones **1** *via* the selenochromenes **2** or **3** is investigated. The properties associated with the stability of the selenopyrylium salts **4** are elucidated.

Introduction

We have performed a series on the syntheses and reactions of the tellurium- or selenium-containing heterocycles,[2,3] especially the seleno- or telluro-pyrylium salts, six-membered heteroaromatic cations containing a selenium or tellurium element in recent years. We have already reported the isolation of the stable novel 2-benzotelluropyrylium salts[4] and 2-benzoselenopyrylium salts.[5] More recently, we have succeeded in the preparation of their structural isomers, the 1-benzotelluropyrylium salts[6] from the corresponding tellurochromen-4-ones,[3] *via* the tellurochromenes and examined their reactions with nucleophiles. It has been found the telluropyrylium salts having a primary alkyl group on the C-2 position could not be isolated due to their instability; they decomposed within approximately 10 minutes during the isolation operation, although the formation of the telluropyrylium salts could be observed by ^{1}H NMR. In addition, the parent unsubstituted telluropyrylium salt could not be synthesized in the method.[6]

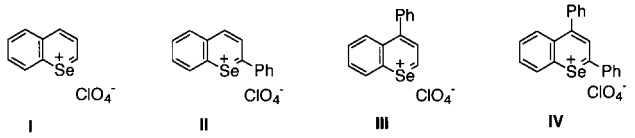
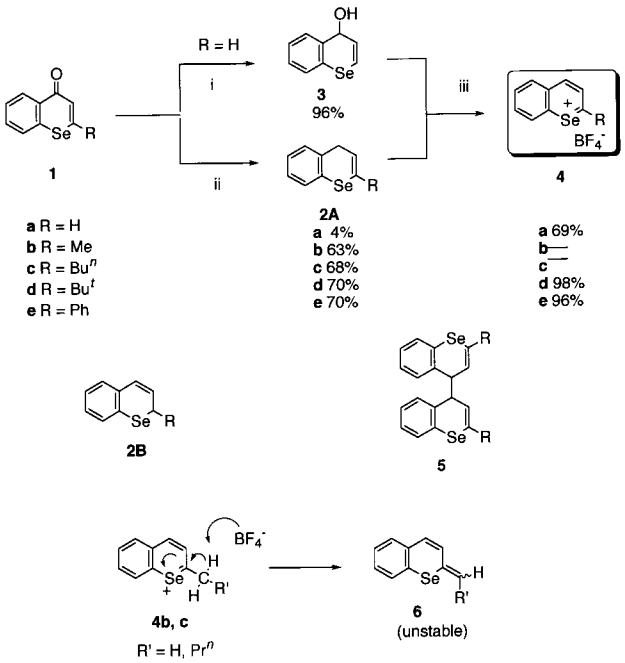


Fig. 1

Regarding their selenium analogues, the 1-benzoselenopyrylium salts, the parent unsubstituted selenopyrylium salt I was prepared first by Degani and co-workers[7] in 1964, and then Renson and co-workers[8] described the synthesis of the 2-phenyl-**II** and 4-phenyl-selenopyrylium salts **III**, which were converted into the 2,4-diphenyl derivative **IV**. These four derivatives of the selenopyrylium salts were isolated as the perchlorates. However, the 1-benzoselenopyrylium salts having an alkyl substituent have never been prepared until now. In addition, it has been reported that a selenopyrylium perchlorate, *i.e.* the 2-benzoselenopyrylium salt obtained from isoselenochromene, explosively decomposes on isolation.[9] In this paper we report the preparation of some non-explosive 1-benzoselenopyrylium salts including the unsubstituted and 2-phenyl derivatives.

Results and discussion

The synthesis of the 1-benzoselenopyrylium salts **4** from the corresponding selenochromen-4-ones **1**[3] is achieved as shown in Scheme 1. Our method for the preparation of the 1-benzoselenopyrylium tetrafluoroborates **4** from **1** is essentially the same as that described for the preparation of the 1-benzotelluropyrylium salts in a previous paper.[6]



Scheme 1 *Reagents and conditions:* i, $NaBH_4$, MeOH, 0 °C; ii, DIBAL-H, *n*-hexane-THF, 0 °C, 1h; iii, $Ph_3C^+ BF_4^-$, $MeNO_2$ or AcOH, room temp., 30 min.

In order to obtain the 4*H*-selenochromenes **2A**, the precursors for the synthesis of the 1-selenopyrylium salts **4**, diisobutylaluminium hydride (DIBAL-H) reduction[10] was used for the reduction of the carbonyl group to the methylene group. The DIBAL-H reduction of **1b–e** in *n*-hexane / THF at 0 °C gave the corresponding 4*H*-selenochromenes **2Ab–e** in good yields (63-70%). However, a similar reduction of the 2-unsubstituted derivative **1a** afforded **2Aa** in a very poor yield (*ca* 4% yield) together with 2*H*-selenochromene **2Ba**, its regioisomer, in 15% yield. Therefore, we selected 4-hydroxy-4*H*-selenochromene **3** as the precursor for the preparation of the 2-unsubstituted selenopyrylium salt **4a**. The $NaBH_4$ reduction of **1a** in MeOH at 0 °C gave the unstable 4-hydroxyselenochromene **3** in almost quantitative yield. Therefore, compound **3** was used for the next step without purification. In the case of the reduction with DIBAL-H or $NaBH_4$ of the selenochromen-4-ones **1**, the 2*H*-selenochromenes **2Bb–e** (as shown by ^{1}H NMR) were never obtained. Also the dimeric products **5** could not be found in the DIBAL-H reduction of **1**, while a similar reduction of the 1-benzotelluropyrylium salts[6] gave the corresponding dimers in 3–8% yields.

Treatment of **2Ab–e** with 1.1 equivalents of triphenylcarbenium tetrafluoroborate ($Ph_3C^+ BF_4^-$) in $MeNO_2$ at room temperature gave the desired 1-benzoselenopyrylium tetrafluoroborates **4b–e**. Salts **4d** and **4e** could easily be precipitated by the addition of dry Et_2O to the $MeNO_2$ solution in almost quantitative yields as yellow prisms. However, the salts

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 ^{1}H NMR spectral data for the 1-benzoselenopyrylium salts **4**

Compound no.	^{1}H NMR δ (400 MHz, CD_3CN)			
	3-H	4-H	Ar-H (5-, 6-, 7-, 8-H)	R-H
4a R = H	8.74 (dd, *J* 9.0, 9.0)	9.59 (d, *J* 9.0)	8.18–8.31 and 8.79–8.92 (4H, m)	11.38 (1H, d, *J* 9.0, 2-H)
4b[a] R = Me	8.42 (d, *J* 9.6)	9.34 (d, *J* 9.6)	8.06–8.78 and 8.67–8.78 (4H, m)	3.27 (3H, s, Me)
4c[a] R = Bu^n	8.45 (d, *J* 10.0)	9.34 (d, *J* 10.0)	8.10–8.19 and 8.67–8.77 (4H, m)	0.91, 1.39–1.63, 3.58 (3H, t, *J* 7.5, 4H, m, 2H, t, *J* 7.9, Bu^n)
4d R = Bu^t	8.72 (d, *J* 10.0)	9.42 (d, *J* 10.0)	8.14–8.27 and 8.71–8.82 (4H, m)	1.71 (9H, s, Bu^t)
4e R = Ph	8.83 (d, *J* 9.9)	9.45 (d, *J* 9.9)	7.52–8.29 (9H, m, Ar-H)	

[a] Not isolated.

4b and **4c** having a primary alkyl group on the C-2 position could not be isolated owing to their instability; **4b** and **4c** decomposed within approximately 10 minutes during the isolation operation, although the formation of the selenopyrylium salts could be observed by ^{1}H NMR. This characteristic behavior of the selenopyrylium salts **4** is fundamentally the same as those of the 1-benzotelluropyrylium salts[6] and 1-benzyl-2-benzotelluropyrylium salts,[4] whose counteranion, BF_4^-, eliminated a β-hydrogen of the methylene group of the primary alkyl group forming the unstable *exo*-methylene compound **6** (Scheme 1). The selenopyrylium salt **4a** was similarly obtained by treatment of the crude 4-hydroxy-4*H*-selenochromene **3** with $Ph_3C^+ BF_4^-$ in acetic acid instead of $MeNO_2$ in 69 % overall yield from **1a** as stable pale green prisms. The ^{1}H NMR spectral data of the 1-benzoselenopyrylium salts **4** are listed in Table 1. Although the salts **4a** (R=H)[7] and **4e** (R=Ph)[8] (the counter-ion for these salts is perchlorate) have been prepared before, the other derivatives **4b** (R=Me), **4c** (R=Bu^n) and (R=Bu^t) are hitherto unknown compounds.

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 HR-MS were recorded on a JEOL JMS-DX300 instrument. ^{1}H NMR spectra were determined with a JEOL PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or 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. ^{13}C NMR spectra and NOE spectra were measured on JEOL JNM-GSX 400 spectrometer. ^{77}Se NMR spectra were recorded on a JEOL EX-400 spectrometer at 76.2 MHz, and samples were referenced to Me_2Se as an external standard.

*General procedure for the synthesis of 4*H*-selenochromenes* **2Ab–e**: A DIBAL-H solution in hexane (0.95 mol/l, 110 ml, 105 mol) was added dropwise with stirring to a solution of 2-substituted selenochromen-4-one **1** (50 mol) in dry THF (100 ml) under an argon atmosphere at 0 °C. The mixture was stirred for an additional 1h, diluted with ether (100 ml). The organic phase was washed with 5 % HCl, saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$) and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane as eluent to give **2A**.

*2-Methyl-4*H*-selenochromene* **2Ab**: Yield 63%, yellow oil; δ_H (90 MHz, $CDCl_3$) 2.21 (3H, d, *J* 2, Me), 3.27 (2H, br d, *J* 4 , 4-H), 6.00 (1H, br t, *J* 4, 3-H), 7.0–7.3 and 7.5–7.6 (3H, m and 1H, m, Ph-H) (HRMS: *m/z* Calc. for $C_{10}H_{10}{}^{80}Se$: 209.9948. Found: 209.9953).

*2-n-Butyl-4*H*-selenochromene* **2Ac**: Yield 68%, yellow oil; δ_H (90 MHz, $CDCl_3$) 0.95, 1.2–2.0 and 2.48 (3H, t, *J* 6, 4H,m, 2H, br t, *J* 7, Bu^n), 3.23 (2H, d, *J* 6, 4-H), 5.98 (1H, br t, *J* 6, 3-H), 7.0–7.3 and (3H, m and 1H, m, Ph-H) (HRMS: *m/z* Calc. for $C_{13}H_{16}{}^{80}Se$: 252.0418. Found: 252.0419).

*2-tert-Butyl-4*H*-selenochromene* **2Ad**: Yield 70%, yellow oil; δ_H (90 MHz, $CDCl_3$) 1.19 (9H, s, Bu^t), 3.21 (2H, d, *J* 6, 4-H), 6.06 (1H, t, *J* 6, 3-H), 7.0–7.3 and 7.5–7.7 (3H, m and 1H, m, Ph-H) (HRMS: *m/z* Calc. for $C_{13}H_{16}{}^{80}Se$: 252.0418. Found: 252.0417).

*2-Phenyl-4*H*-selenochromene* **2Ae**: Yield 70%, yellow prisms, m.p. 77–78 °C (from acetone -hexane); *m/z* 272 (M^+); δ_H (90 MHz, $CDCl_3$) (2H, d, *J* 5, 4-H), 6.42 (1H, t, *J* 5, 3-H), 7.1–7.6 (9H, m, Ph-H) (Anal: Calc. for $C_{15}H_{12}Se$: C, 66.43; H, 4.46. Found: C, 66.41; H, 4.40%).

*4-Hydroxy-4*H*-selenochromene* **3**: $NaBH_4$ (1.34 g) was added in a small portion with stirring to a solution of selenochromen-4-ones **1a** (2.10 g, 10 mol) in dry MeOH (25 ml) under an argon atmosphere at 0 °C. The mixture was stirred for an additional 1h and extracted with CH_2Cl_2 (100 ml × 3). The organic layers were washed with brine and dried ($MgSO_4$), and evaporated *in vacuo* to give **3** (2.04 g, 96%), yellow oil; δ_H (90 MHz, $CDCl_3$) 4.8 (1H, m, 4-H), 5.0 (1H, br, OH), 6.42 (1H, dd, *J* 8 and 4, 3-H), 6.97 (1H, d, *J* 8, 2-H), 7.1–7.8 (4H, m, Ph-H) (HRMS: *m/z* Calc. for $C_9H_8O^{80}Se$: 211.9741. Found: 211.9751).

1-Benzoselenopyrylium tetrafluoroborate **4a**: $Ph_3C^+ BF_4^-$ (3.63g, 11 mmol) was added in one portion to a stirred solution of **3** (2.12 g, 10 mmol) in AcOH (25 ml) and the mixture was stirred at room temperature for 30 min. To the reaction mixture was added dry ether (200 ml) to precipitate the selenopyrylium salt **4a** (1.39 g, 69%) as pale green prisms (from $CHCl_3$), m.p. 99–101 °C; ν_{max} (KBr)/cm^{-1} 1036 (BF_4^-); δ_C (100 MHz, CD_3CN) 131.5 (d), 132.4 (d), 133.7 (s), 134.3 (d), 135.5 (d), 138.6 (d), 153.5 (s), 155.2 (d), 177.3(d) (Anal: Calc. for $C_9H_7BF_4Se$: C, 38.48; H, 2.51. Found: C, 38.40; H, 2.54%).

2-tert-butyl-1-benzoselenopyrylium tetrafluoroborate **4d**: $Ph_3C^+ BF_4^-$ (3.63g, 11 mmol) was added in one portion to a stirred solution of **2Ad** (2.72 g, 10 mmol) in $MeNO_2$ (20 ml) and the mixture was stirred at room temperature for 30 min. To the reaction mixture was added dry ether (200 ml) to precipitate the selenopyrylium salt **4d** (3.03 g, 98%), as pale yellow prisms (from $CHCl_3$), m.p. 172–174 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1064 (BF_4^-) δ_C (CD_3CN, 100 MHz) 29.9 (q), 45.1 (s), 129.6 (d), 129.8 (d), 130.7 (s), 132.6 (d), 134.1 (d), 136.3 (d), 149.1 (s), 153.3 (d), 212.5 (d); δ_{Se} (CD_3CN) 852.4 (Anal: Calc. for $C_{13}H_{15}BF_4Se$: C, 46.33; H, 4.49. Found: C, 46.24; H, 4.38%).

2-Phenyl-1-benzoselenopyrylium tetrafluoroborate **4e**: The selenochromene **2Ae** was treated with $Ph_3C^+ BF_4^-$ and worked up as described for the preparation of **4d** to give **4e** (3.42 g, 96%) as yellow prisms (from $CHCl_3$), m.p. 140–145 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1056 (BF_4^-); δ_C (CD_3CN, 100 MHz) 130.1 (d), 130.7 (d), 130.8 (d), 131.9 (d), 132.2 (s), 133.9 (d), 135.8 (d), 136.5 (d), 138.1 (d), 138.1 (s), 150.7 (s), 155.2 (d), 192.3 (s). (Anal: Calc. for $C_{15}H_{11}BF_4Se$: C, 50.46; H, 3.11. Found: C, 50.22; H, 2.97%).

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