Studies on tellurium-containing heterocycles. Part 12.[1] 2-Substituted 1-benzotelluropyrylium salts: synthesis and reactions with nucleophiles

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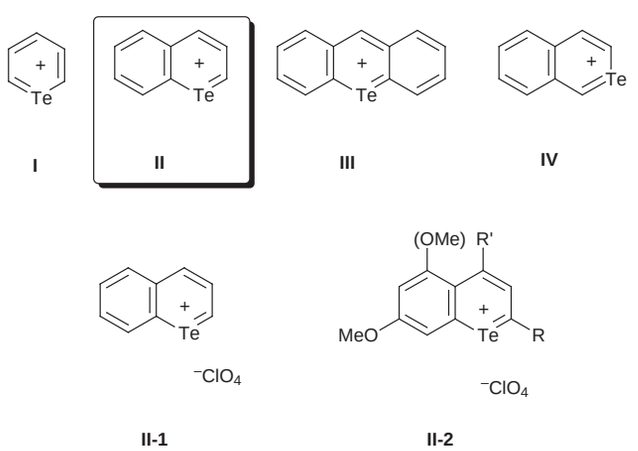
Received (in Cambridge) 19th March 1999, Accepted 23rd April 1999

The general preparation of 2-substituted 1-benzotelluropyrylium salts **3** from the tellurochromen-4-ones **1** in two steps is outlined. The sensitive stability to the nature of the substituents at the C-2 position and the reactions with several nucleophiles including OMe^-, diethylamine, CN^-, an active methyl compound (acetone) and $PhCH_2MgBr$, and also hydrogenation and hydrolysis reactions are described.

Introduction

In recent years, the chemistry of the telluropyrylium salts,[2] six-membered heterocyclic cations containing a tellurium element, has attracted much attention when comparing them to thio- and seleno-pyrylium salts.[3] Monocyclic **I**,[4] benzene ring-fused **II**[4b,5] and dibenzo derivative **III**[6] were prepared, and their reactivities have also been examined to a limited extent. As regards the 1-benzotelluropyrylium salts **II**, the parent pyrylium skeleton **II-1** was synthesized as the perchlorate salt from the corresponding chromene by Nivorozhkin and Sadekov[5a] in 1986. Detty and Murray[5b] have reported the preparation of several derivatives of **II-2** having a methoxy group on the benzene ring, and described the condensation reactions[4a,c] of 2-alkyl- or 4-alkyl-substituted telluropyrylium salts with carbonyl-containing compounds. However, the reactivities of the simple ring system of 1-benzotelluropyrylium salts **II**, in particular towards nucleophiles has scarcely been examined because Detty and Luss' method for the synthesis of tellurochromen-4-ones, the precursors for the preparation of the telluropyrylium salts **II-2**, is the Friedel–Crafts reactions of β-(aryltelluro)cinnamoyl chlorides.[5b] The chromen-4-ones could only be obtained in the presence of a strong electron-donating group such as OMe at the C-7 and (or) C-5 positions on the benzene ring.

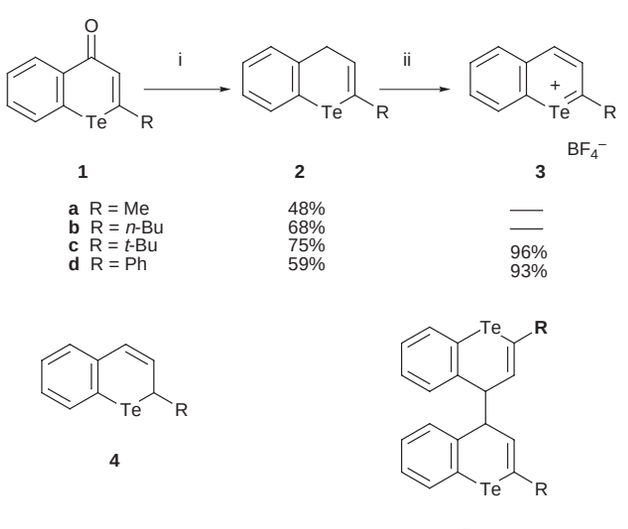


On the other hand, we have recently extensively studied the syntheses and reactions of tellurium- and selenium-containing heterocycles,[7] and further reported the general synthetic method for the preparation of the tellurochromen-4-ones **1**.[8] More recently, we have succeeded in the preparation of the theoretically possible structural isomer of **II**, 2-benzotelluro- **IV**,[9] and the preparation of 2-benzoseleno-pyrylium salts,[10] and described their reactions with several nucleophiles. In our continuing studies, this paper describes the synthesis of the title compounds, and their reactions with several nucleophiles, hydride reductions and hydrolyses.

Results and discussion

Synthesis of 1-benzotelluropyrylium salts

The synthesis of the 1-benzotelluropyrylium salts **3** from the corresponding tellurochromen-4-ones **1**[8] is shown in Scheme 1.



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

In order to obtain the tellurochromenes **2**, the precursors for the preparation of the 1-benzotelluropyrylium salts **3**, diisobutylaluminium hydride (DIBAL-H) reduction, reported by Detty and co-workers,[4b,5b] was used for the conversion of the carbonyl group to the methylene group of **2**. The DIBAL-H reduction of **1** gave the 4*H*-tellurochromenes **2** in yields ranging from 48 to 75%. The 4*H*-chromenes **2** were free from

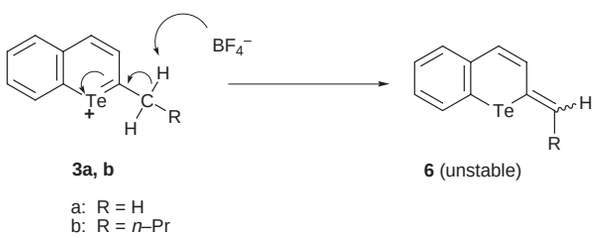
Table 1 ^{1}H NMR data for the 1-benzotelluropyrylium salts **3**

Compound no.	δ_H (400 MHz, CD_3CN) 3-H	4-H	Ph-H (5-, 6-, 7-, 8-H)	R
3a[a]	8.40	9.39	7.93–8.03 (2H, m)	3.15 (3H, s, Me)
R = Me	(d, *J* 9.9)	(d, *J* 9.9)	8.80–8.95 (2H, m)	
3b[a]	8.46	9.42	7.90–8.06 (2H, m)	0.99, 1.27–1.74, 2.44–2.60 (3H,
R = Bu^n	(d, *J* 9.6)	(d, *J* 9.6)	8.86–8.91 (2H, m)	*J* 6.6, 4H, m, 2H, m, Bu^n)
3c	8.76	9.50	7.98–8.09 (2H, m)	1.68 (9H, s, Bu^t)
R = Bu^t	(d, *J* 10.2)	(d, *J* 10.2)	8.81–8.93 (2H, m)	
3d	8.80	9.49	7.48–8.07 (7H, m)	
R = Ph	(d, *J* 10.2)	(d, *J* 10.2)	8.90–9.01 (2H, m, Ph)	

[a] Not isolated.

their regioisomers **4** (as shown by ^{1}H NMR), while the dimeric products **5** (as shown by MS) were determined to form in approximately 3–8% yields.

Treatment of 2-*tert*-butyl- **2c** and 2-phenyl-tellurochromenes **2d** with 1.05 equivalents 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-benzotelluropyrylium tetrafluoroborates **3c** and **3d** respectively in almost quantitative isolated yields as stable yellow prisms. However, similar treatment of the chromenes **2a** and **2b** having a primary alkyl group at the C-2 position did not afford the corresponding stable products. Salts **3a** and **3b** could not be isolated, although the formation of the salts could be observed by ^{1}H NMR. This distinction between a primary alkyl group and other carbon functionalities at the C-2 position with respect to the stability of the telluropyrylium salts **3** is explained below (Scheme 2). BF_4^-,



Scheme 2

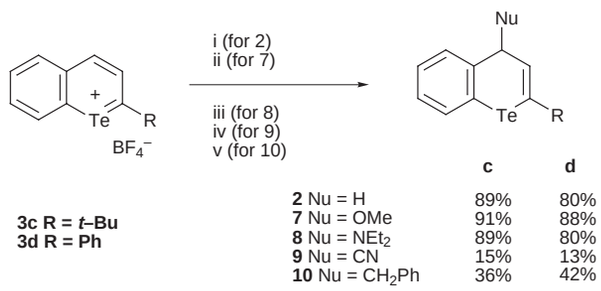
the counter anion of the salts **3**, eliminated the β-hydrogen of the methylene carbon of the primary alkyl group forming the unstable *exo*-methylene compound **6**. Salts **3a** and **3b** decomposed within approximately 3–5 minutes during the isolation operation. In our previous paper,[9] we observed the elimination of the β-hydrogen of the benzyl group in the 1-benzyl-2-benzotelluropyrylium salts. Table 1 shows the ^{1}H NMR spectral data of the telluropyrylium salts **3**. All products **3a**–**d** were hitherto unknown compounds.

Reactions of 1-benzotelluropyrylium salts

Next, we examined the reactivities of the telluropyrylium salts **3** towards nucleophiles using the stable isolated substrates **3c** and **3d**.

$LiAlH_4$ reduction of **3** in THF gave the 4*H*-tellurochromenes **2c** and **2d** in 89 and 80% yields respectively, as isomerically pure compounds. It was found that the major products from the $NaBH_4$ reduction of **3c** and **3d** in MeOH were surprisingly the 4-methoxy-4*H*-tellurochromenes **7c** and **7d** and not the reduced products (Scheme 3). This fact indicates that MeOH operated as a nucleophile towards the telluropyrylium salts **3**. Indeed, treatment of **3** with NaOMe in MeOH afforded **7** in high yields as the sole characterized products. However, secondary (*e.g.* propan-2-ol) and tertiary alcohols (*e.g. tert*-butyl alcohol) alongside the corresponding alkoxide did not react completely.

The telluropyrylium salts **3** had high reactivities and normally



Scheme 3 *Reagents and conditions*: i, $LiAlH_4$, THF, 0 °C, 30 min; ii, NaOMe, MeOH, room temp., 30 min; iii, $HNEt_2$, benzene, room temp., 30 min; iv, KCN, 18-crown-6, MeCN, room temp., 2 h; v, $PhCH_2MgBr$, ether, 0 °C, 30 min.

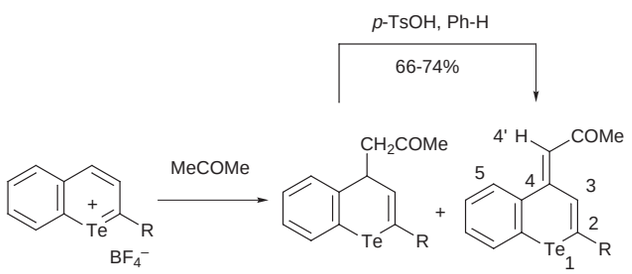
reacted with other nucleophiles. The reaction of the salts **3** with diethylamine in benzene at room temperature also resulted in nucleophilic addition at the C-4 position to afford the 4-diethylamino-4*H*-tellurochromenes **8c** and **8d** in 89 and 80% yields, respectively. Products **7** and **8** were isolated in a nearly pure state but decomposed during silica gel chromatography. Moreover, nucleophilic attack of a cyanide ion (KCN), in the presence of 18-crown-6 as a phase transfer catalyst in MeCN, at the C-4 position was carried out to produce the 4-cyano-4*H*-tellurochromenes **9** as pure compounds. The length of the reaction reduced the yields of the products due to their instability.

In order to obtain products having different carbon functional groups at the C-4 position, the Grignard reaction with salt **3** was carried out. However, the results were disappointing. Treatment of **3** with Grignard reagents, such as methyl-, ethyl- and phenyl-magnesium bromide (iodide) resulted in decomposition of the starting material to give a complex mixture including a small quantity of the dimeric products **5** (as shown by MS). In contrast use of benzylmagnesium bromide as a Grignard reagent in Et_2O at 0 °C gave 4-benzyl-4*H*-tellurochromenes **10**, as normal coupling products in moderate yields. In this case, no dimers **5** were formed. Similar behavior has been observed in the reaction of the 2-benzotelluropyrylium salts[9] with Grignard reagents which lead to dimeric products except in the case of 1-benzyl-2-benzotelluropyrylium salts. In all the cases described above, none of the nucleophiles attacked **3** at the C-2 position and no 4-substituted 2*H*-tellurochromenes were produced.

Furthermore, the salts **3c** and **3d** readily reacted with dry acetone even at room temperature in analogy with 2-benzotelluropyrylium salts.[9] This is in spite of the absence of an electron-withdrawing group,[11] which enhances the reactivity of the pyrylium ring. 4-Acetonyl-2-*tert*-butyl-4*H*-tellurochromene **11c** and (*E*)-4-acetonylidene-4*H*-tellurochromene **12c** were obtained in 19 and 28% yields, respectively; the former is probably the initial product, and was easily dehydrogenated to afford **12c** by refluxing in the presence of toluene-*p*-sulfonic acid (TsOH) in benzene (Scheme 4). Heating of **11** in benzene

Table 2 Spectral data for the 4*H*-isotellurochromenes **2**, **5**–**8**

Compound no.	Molecular formula MS (M^+)	δ_H (90 MHz, $CDCl_3$) 3-H	4-H	4-Nu	Ph-H (5-, 6-, 7-, 8-H)	R
2a	$C_{10}H_{10}Te$	6.11	3.24		6.9–7.4 (3H, m)	2.16
Nu = H	260	(br t, *J* 6)	(2H, br d, *J* 6)		7.70 (1H, d, *J*, 7)	(3H, br s, Me)
2b	$C_{13}H_{16}Te$	6.16	3.24		6.9–7.4 (3H, m)	0.90, 1.2–1.6, 2.60
Nu = H	302	(t, *J* 6)	(2H, d, *J* 6)		7.72 (1H, d, *J* 7)	(3H, t, *J* 6, 4H, m, 3H, t, *J* 6, Bu^n)
2c	$C_{13}H_{16}Te$	6.18	3.28		7.0–7.5 (3H, m)	1.22 (9H, s, Bu^t)
Nu = H	302	(t, *J* 6)	(2H, d, *J* 6)		7.78 (1H, d, *J* 7)	
2d	$C_{15}H_{12}Te$	6.50	3.44		6.9–7.5 (8H, m)	
Nu = H	322	(t, *J* 6)	(2H, d, *J* 6)		7.73 (1H, d, *J* 7, Ph)	
5c	$C_{14}H_{18}OTe$	6.20	4.06	3.63	7.0–7.9	1.20 (9H, s, Bu^t)
Nu = OMe	332	(d, *J* 3)	(d, *J* 3)	(3H, s)	(4H, m)	
5d	$C_{16}H_{14}OTe$	6.56	4.27	3.64	7.1–7.9	
Nu = OMe	352	(d, *J* 3)	(d, *J* 3)	(3H, s)	(9H, m)	
6c	$C_{17}H_{25}NTe$	6.23	3.76	1.17, 2.76	6.9–7.8	1.23 (9H, s, Bu^t)
Nu = NEt_2	373	(d, *J* 4)	(d, *J* 4)	(6H, t, *J* 6, 4H, q, *J* 6)	(4H, m)	
6d	$C_{19}H_{21}NTe$	6.67	4.07	1.20, 2.80	6.9–7.8	
Nu = NEt_2	393	(d, *J* 4)	(d, *J* 4)	(6H, t, *J* 7, 4H, q, *J* 7)	(9H, m)	
7c	$C_{14}H_{15}NTe$	6.18	3.90	—	7.1–7.9	1.27 (9H, s, Bu^t)
Nu = CN	327	(d, *J* 4)	(d, *J* 4)		(4H, m)	
7d	$C_{16}H_{11}NTe$	6.53	4.17	—	7.3–8.0	
Nu = CN	347	(d, *J* 4)	(d, *J* 4)		(9H, m)	
8c	$C_{20}H_{22}Te$	5.99	3.45	3.03, 3.37 (each 1H, d, *J* 7)		1.09 (9H, s, Bu^t)
Nu = CH_2Ph	392	(d, *J* 5)	(ddd, *J* 5, 7, 7)	6.9–7.4, 7.7–7.8 (8H, m, 1H, m, Ph-H)		
8d	$C_{22}H_{18}Te$	6.33	3.73	3.05, 3.45 (each 1H, d, *J* 6)		
Nu = CH_2Ph	412	(d, *J* 6)	(ddd, *J* 6, 6, 6)	6.9–7.5, 7.6–7.8 (13H, m, 1H, m)		



Scheme 4

in the absence of TsOH and oxygen resulted in the gradual decomposition of the starting material without affording any products. The stereochemistry of the acetonylidene moiety of **12** was determined by the nuclear Overhauser enhancement (NOE) measurement. The NOE was observed between the 4′-H and aromatic 5-H in the ^{1}H-NMR spectrum of **12c**. Thus, the olefin moiety was determined to have (*E*)-stereochemistry. Similarly, **11d** and **12d** were obtained from **3d**.

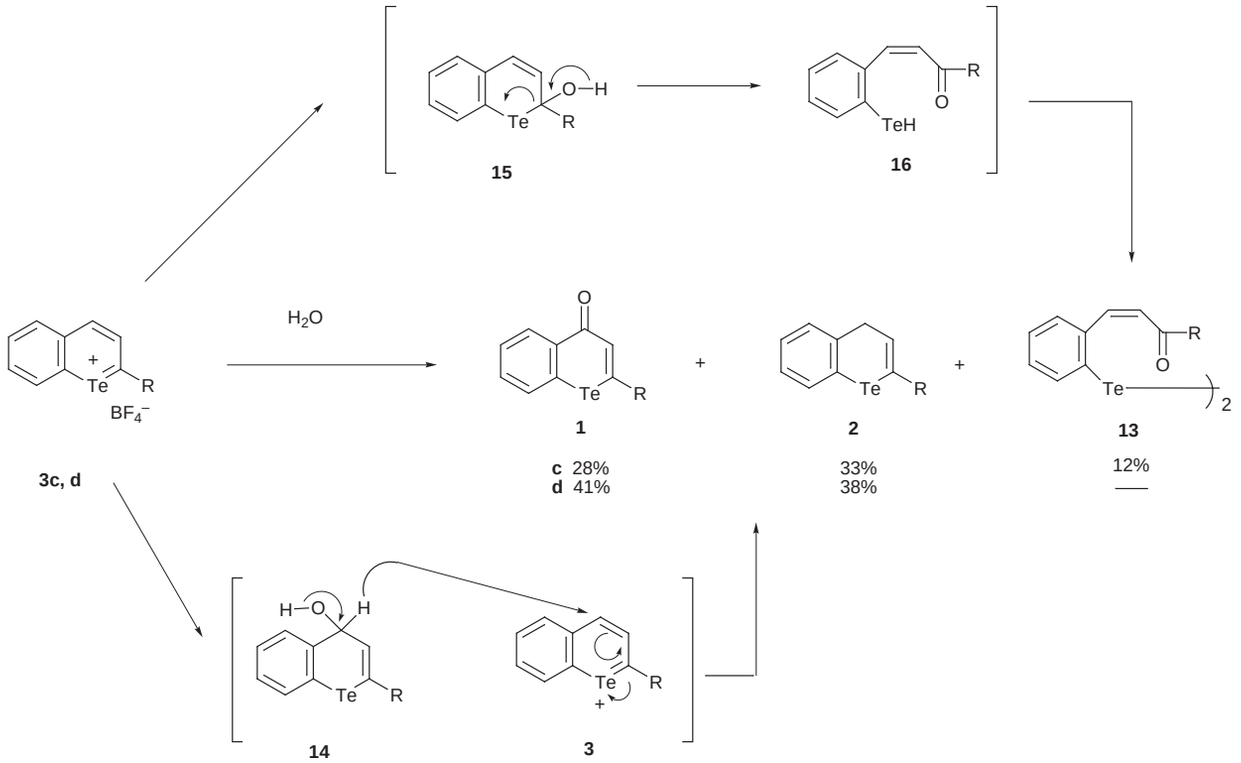
The hydrolysis[2,12] of the monocyclic telluropyrylium salts **I** was reported to replace tellurium by oxygen as the cationic atom. So, we examined the hydrolysis of the 1-benzotelluropyrylium salts **3**. Treatment of salt **3c** with water containing a small amount of potassium ferricyanide yielded the diphenyl ditelluride **13c**, the tellurochromen-4-one **1c**, and the 4*H*-tellurochromene **2c** in 12, 28, and 33% yields, respectively. It is already well known[13] that oxidation of phenyltellurol gives diphenyl ditelluride. Thus, a possible mechanism for the formation of **13** is shown in Scheme 5. The initial intermediate, 2-hydroxy-2-*tert*-butyl-2*H*-tellurochromene **15**, generated by nucleophilic attack of water at the C-2 position of **3c**, undergoes ring opening with migration of the hydroxy proton to form the phenyltellurol **16**. The resulting tellurol **16** is oxidized by air or potassium ferricyanide to give the ditelluride **13c**. The MS spectrum of this compound suggested the ditelluride molecular formula of $C_{26}H_{30}O_2Te_2$ as it recorded a molecular ion at *m*/*z* = 634 (^{130}Te) and the expected isotope pattern for Te_2. In addition the HRMS of **13c** showed the exact molecular formula. The formation of **1c** and **2c** might be explained by the process involving an intermolecular hydride shift from the 4-hydroxytellurochromene **14** to the parent 1-benzotelluropyrylium cation **3**, analogous with the hydrolysis of the 2-phenylthiopyrylium salt.[14] In the case of the hydrolysis of the 2-phenyl derivative **3d**, the chromen-4-one **1d** (41% yield) and the chromene **2d** (38% yield) were obtained without producing the diphenyl ditelluride. This mechanism for the formation of **1** and **2** is supported by the fact that both compounds of **1** and **2** are produced in approximately equal yields.

Conclusions

In the present work, synthesis of the 2-substituted-1-benzotelluropyrylium salts without a OMe group on the benzene ring was achieved. The properties associated with the stability of the salts were elucidated. 4*H*-Tellurochromenes with a functional group at the C-4 position were obtained by the reaction of the parent salts with several nucleophiles. Further reactions and applications of the telluropyrylium salts are now under investigation.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Hitachi 270-30 spectrometer. Mass spectra (MS) and HRMS were recorded on a JEOL JMS-DX300 instrument. ^{1}H NMR spectra were recorded on a JEOL PMX-60 SI (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 a JEOL JNM-GSX 400 spectrometer. ^{125}Te NMR spectra were recorded on a JEOL EX-400 spectrometer at 126.1 MHz, and samples were referenced to $^{125}TeMe_2$ as an external standard.



Scheme 5

General procedure for the synthesis of 4*H*-tellurochromenes 2

DIBAL-H hexane solution (0.95 mol l^{-1}, 22.1 ml, 21 mmol) was added dropwise with stirring to a solution of the tellurochromen-4-one **1** (10 mmol) in dry THF (20 ml) under an argon atmosphere at 0 °C. The mixture was stirred for 1 h and diluted with Et_2O (100 ml). The organic layers were washed with 5% HCl and saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and evaporated *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane as eluent to give **2**. The spectral data are collected in Table 2.

2-Methyl-4*H*-tellurochromene 2a. Yield 48%, pale yellow oil (HRMS *m*/*z* Calc. for $C_{10}H_{10}Te$: 259.9845. Found: 259.9847).

2-*n*-Butyl-4*H*-tellurochromene 2b. Yield 68%, yellow oil (HRMS *m*/*z* Calc. for $C_{13}H_{16}Te$: 302.0315. Found: 302.0316).

2-*tert*-Butyl-4*H*-tellurochromene 2c. Yield 75%, yellow oil (HRMS *m*/*z* Calc. for $C_{13}H_{16}Te$: 302.0315. Found: 302.0316).

2-Phenyl-4*H*-tellurochromene 2d. Yield 59%, yellow prisms, mp 75–76 °C from acetone–*n*-hexane; MS *m*/*z* 322 (M^+) (Anal. Calc. for $C_{15}H_{12}Te$: C, 56.33; H, 3.78. Found: C, 56.23; H, 3.73%).

2-*tert*-Butyl-1-benzotelluropyrylium tetrafluoroborate 3c

Ph_3C^+ BF_4^- (1.80 g, 5.25 mmol) was added to a stirred solution of the tellurochromene **2c** (1.51 g, 5 mmol) in dry $MeNO_2$ (10 ml) and the mixture was stirred at room temperature for 30 min. To the reaction mixture was added dry Et_2O (*ca*. 100 ml) to precipitate the telluropyrylium salt **3c** (1.85 g, 96%), yellow prisms ($CHCl_3$), mp 158–159 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1064 (BF_4^-); δ_C (CD_3CN, 100 MHz) 31.9 (q), 48.8 (s), 133.1 (d), 133.5 (s), 133.7 (d), 134.8 (d), 136.3 (d), 140.0 (d), 146.1 (s), 154.7 (d), 226.2 (s); δ_{Te} (CD_3CN) 1221.7 (Anal. Calc. for $C_{13}H_{15}BF_4Te$: C, 40.49; H, 3.93. Found: C, 40.25; H, 3.75%).

2-Phenyl-1-benzotelluropyrylium tetrafluoroborate 3d

The tellurochromene **2d** was treated with Ph_3C^+ BF_4^- and worked up as described for the preparation of **3c** to give **3d** (1.86 g, 92%), orange prisms ($CHCl_3$) mp 134–137 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1054 (BF_4^-); δ_C (CD_3CN, 100 MHz) 129.5 (d), 131.7 (d), 133.2 (d), 133.5 (d), 133.7 (s), 134.4 (d), 135.5 (d), 135.9 (d), 140.4 (s), 143.1 (s), 150.3 (s), 154.9 (d), 202.2 (s) (Anal. Calc. for $C_{15}H_{11}BF_4Te$: C, 44.41; H, 2.73. Found: C, 44.11; H, 2.59%).

$LiAlH_4$ reduction of telluropyrylium salts 3

$LiAlH_4$ (16 mg, 0.33 mmol) was added in small portions to a suspended mixture of **3** (0.3 mmol) in THF (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 saturated 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 tellurochromene **2**. The products were identical with authentic samples.

2-*tert*-Butyl-4*H*-tellurochromene 2c. Yield 89%.

2-Phenyl-4*H*-tellurochromene 2d. Yield 80%.

Treatment of telluropyrylium salts 3 with MeOH

NaOMe (28% MeOH solution, 1 ml) was added to a solution of the pyrylium salt **3** (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*. Products were obtained in a nearly pure form, and decomposed during the attempted purification by silica gel chromatography.

2-*tert*-Butyl-4-methoxy-4*H*-tellurochromene 7c. Yield 91%, yellow oil (HRMS *m*/*z* Calc. for $C_{14}H_{18}OTe$: 332.0421. Found: 332.0407).

4-Methoxy-2-phenyl-4*H*-tellurochromene 7d. Yield 88%, yellow oil (HRMS *m*/*z* Calc. for $C_{16}H_{14}OTe$: 352.0108. Found: 352.0114).

Treatment of the pyrylium salts 3 with $HNEt_2$

$HNEt_2$ (0.6 ml) was added slowly to a suspended mixture of **3** (0.3 mmol) in benzene (10 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). The benzene layer was washed with 5% H_2SO_4 (30 ml × 2) and brine (30 ml × 2), dried ($MgSO_4$), and evaporated *in vacuo.* These products were also obtained in nearly pure states, and decomposed during the attempted purification by silica gel chromatography.

2-*tert*-Butyl-4-diethylamino-4*H*-tellurochromene 8c. Yield 89%, yellow oil (HRMS *m*/*z* Calc. for $C_{17}H_{25}NTe$: 373.1050. Found: 373.1057).

4-Diethylamino-2-phenyl-4*H*-tellurochromene 8d. Yield 80%, yellow oil (HRMS *m*/*z* Calc. for $C_{19}H_{21}NTe$: 393.0737. Found: 393.0719).

Treatment of the pyrylium salts 3 with KCN

The pyrylium salt **3** (0.3 mmol) was dissolved in acetonitrile (6 ml) at 0 °C under an argon atmosphere. KCN (39 mg, 0.6 mmol) and 18-crown-6 (12 mg) were added in one portion to the mixture, and the reaction mixture was stirred for 2 h. The mixture was extracted with Et_2O (30 ml × 3). The organic layers were washed with brine (30 ml × 2), dried ($MgSO_4$) and evaporated *in vacuo*. The resulting residue was chromatographed on silica gel with *n*-hexane–CH_2Cl_2 (5 : 2) as eluent to give **9**.

2-*tert*-Butyl-4-cyano-4*H*-tellurochromene 9c. Yield 15%, pale yellow oil; ν_{max} (neat)/cm^{-1} 2250 (CN) (HRMS *m*/*z* Calc. for $C_{14}H_{15}NTe$: 327.0267. Found: 327.0247).

4-Cyano-2-phenyl-4*H*-tellurochromene 9d. Yield 13%, yellow oil; ν_{max} (neat)/cm^{-1} 2210 (CN) (HRMS *m*/*z* Calc. for $C_{16}H_{11}NTe$: 346.9954. Found: 346.9930).

Reaction of telluropyrylium salts 3 with $PhCH_2MgBr$

$PhCH_2MgBr$ (4 mmol) in ether solution (4 ml) was slowly added to a suspended mixture of the pyrylium salt **3** (3 mmol) in ether (20 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred under these 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), dried ($MgSO_4$) and evaporated *in vacuo.* The resulting residue was chromatographed on silica gel, with *n*-hexane–CH_2Cl_2 (20 : 1) as eluent to give **10**.

4-Benzyl-2-*tert*-butyl-4*H*-tellurochromene 10c. Yield 36%, yellow oil (HRMS *m*/*z* Calc. for $C_{20}H_{22}Te$: 392.0785. Found: 392.0786).

4-Benzyl-2-phenyl-4*H*-tellurochromene 10d. Yield 42%, yellow oil (HRMS *m*/*z* Calc. for $C_{22}H_{18}Te$: 412.0472. Found: 412.0475).

Treatment of telluropyrylium salts 3 with acetone

The pyrylium salt **3** (0.3 mmol) was dissolved 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 diluted with CH_2Cl_2 (*ca*. 50 ml). The organic layers were washed with brine (30 ml × 2), dried ($MgSO_4$) and evaporated *in vacuo.* The resulting residue was chromatographed on silica gel with *n*-hexane–CH_2Cl_2 (1 : 1) as eluent to give **11** and **12**.

4-Acetonyl-2-*tert*-butyl-4*H*-tellurochromene 11c. Yield 19%, yellow oil; ν_{max}(neat)/cm^{-1} 1724 (C=O); δ_H ($CDCl_3$) 1.19 (9H, s, Bu^t), 2.10 (3H, s, CH_2COCH_3), 2.85 and 3.18 (each 1H, d, *J* 6, CH_2COCH_3), 3.77 (1H, ddd, *J* 6, 6 and 6, 4-H), 6.05 (1H, d, *J* 6, 3-H), 6.9–7.3 and 7.5–7.7 (3H, m and 1H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{16}H_{20}OTe$: 358.0577. Found: 358.0570).

(*E*)-4-Acetonylidene-2-*tert*-butyl-4*H*-tellurochromene 12c. Yield 28%, yellow oil; ν_{max}(neat)/cm^{-1} 1720 (C=O); δ_H ($CDCl_3$) 1.34 (9H, s, Bu^t), 2.30 (3H, s, CH_2COCH_3), 6.36 (1H, s, 3-H), 7.1–7.4 and 7.6–7.9 (2H, m and 2H, m, Ph-H), 8.27 (1H, s, 4′-H) (HRMS *m*/*z* Calc. for $C_{16}H_{18}OTe$: 356.0421. Found: 356.0423).

4-Acetonyl-2-phenyl-4*H*-tellurochromene 11d. Yield 20%, yellow oil; ν_{max}(neat)/cm^{-1} 1716 (C=O); δ_H ($CDCl_3$) 2.10 (3H, s, CH_2COCH_3), 2.85 and 3.37 (1H, d, *J* 6 and 1H, d, *J* 7, CH_2COCH_3), 4.03 (1H, ddd, *J* 6, 6 and 7, 4-H), 6.47 (1H, d, *J* 6, 3-H), 7.1–7.9 (9H, m, Ph-H) (HRMS *m*/*z* Calc. for $C_{18}H_{16}OTe$: 378.0264. Found: 378.0257).

(*E*)-4-Acetonylidene-2-phenyl-4*H*-tellurochromene 12d. Yield 22%, yellow oil; ν_{max}(neat)/cm^{-1} 1716 (C=O); δ_H ($CDCl_3$) 2.33 (3H, s, CH_2COCH_3), 6.45 (1H, s, 3-H), 7.1–7.8 (9H, m, Ph-H), 8.65 (1H, s, 4′-H) (HRMS *m*/*z* Calc. for $C_{18}H_{14}OTe$: 376.0108. Found: 376.0101).

Conversion of 11 to 12

A mixture of **11** (30 mg) and $TsOH{\cdot}H_2O$ (5 mg) in benzene (20 ml) was refluxed with stirring for 1 h. After cooling, the mixture was washed with 5% $NaHCO_3$ (20 × 2), brine (20 ml × 2), dried ($MgSO_4$) and evaporated *in vacuo.* The resulting residue was chromatographed on silica gel with *n*-hexane–CH_2Cl_2 (1 : 1) as eluent to give **12**.

12c. Yield 66%.

12d. Yield 74%.

Hydrolysis of telluropyrylium salts 3

H_2O (6 ml) was added to a suspended solution of the pyrylium salts **3** (0.3 mmol) in Et_2O (12 ml). The reaction mixture was vigorously stirred at room temperature for 30 min, and extracted with Et_2O (50 ml × 3). The organic layer was washed with brine (30 ml × 2), dried ($MgSO_4$) and evaporated *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane–CH_2Cl_2 (2 : 1) as eluent to give **1**, **2**, and **13**. The chromen-4-ones **1** and the chromenes **2** were identical with authentic samples.

2-*tert*-Butyl-4*H*-tellurochromen-4-one 1c. Yield 28%.

2-*tert*-Butyl-4*H*-tellurochromene 2c. Yield 33%.

Bis[*o*-(4,4-dimethyl-3-oxopent-1-enyl)phenyl] ditelluride 13c. Yield 12%, yellow oil; ν_{max} (neat)/cm^{-1} 1686 (C=O); δ_H ($CDCl_3$) 1.22 (18H, s, Bu^t × 2), 6.95 (2H, d, *J* 15, 2- and 2′-H), 7.98 (2H, d, *J* 15, 1- and 1′-H), 7.2–7.5 (8H, m, Ph-H × 2) (HRMS *m*/*z* Calc. for $C_{26}H_{30}O_2Te_2$: 634.0374. Found: 634.0346).

2-Phenyl-4*H*-tellurochromen-4-one 1d. Yield 41%.

2-Phenyl-4*H*-tellurochromene 2d. Yield 38%.

Acknowledgements

The authors wish to express their thanks to Professor K. Akiba and Dr M. Minoura, Hiroshima University for the ^{125}Te NMR spectral measurements.

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