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A SIMPLE AND PRACTICAL PREPARATION OF 2,4-DISUBSTITUTED 1-BENZOTELLUROPYRYLIUM SALTS[1]

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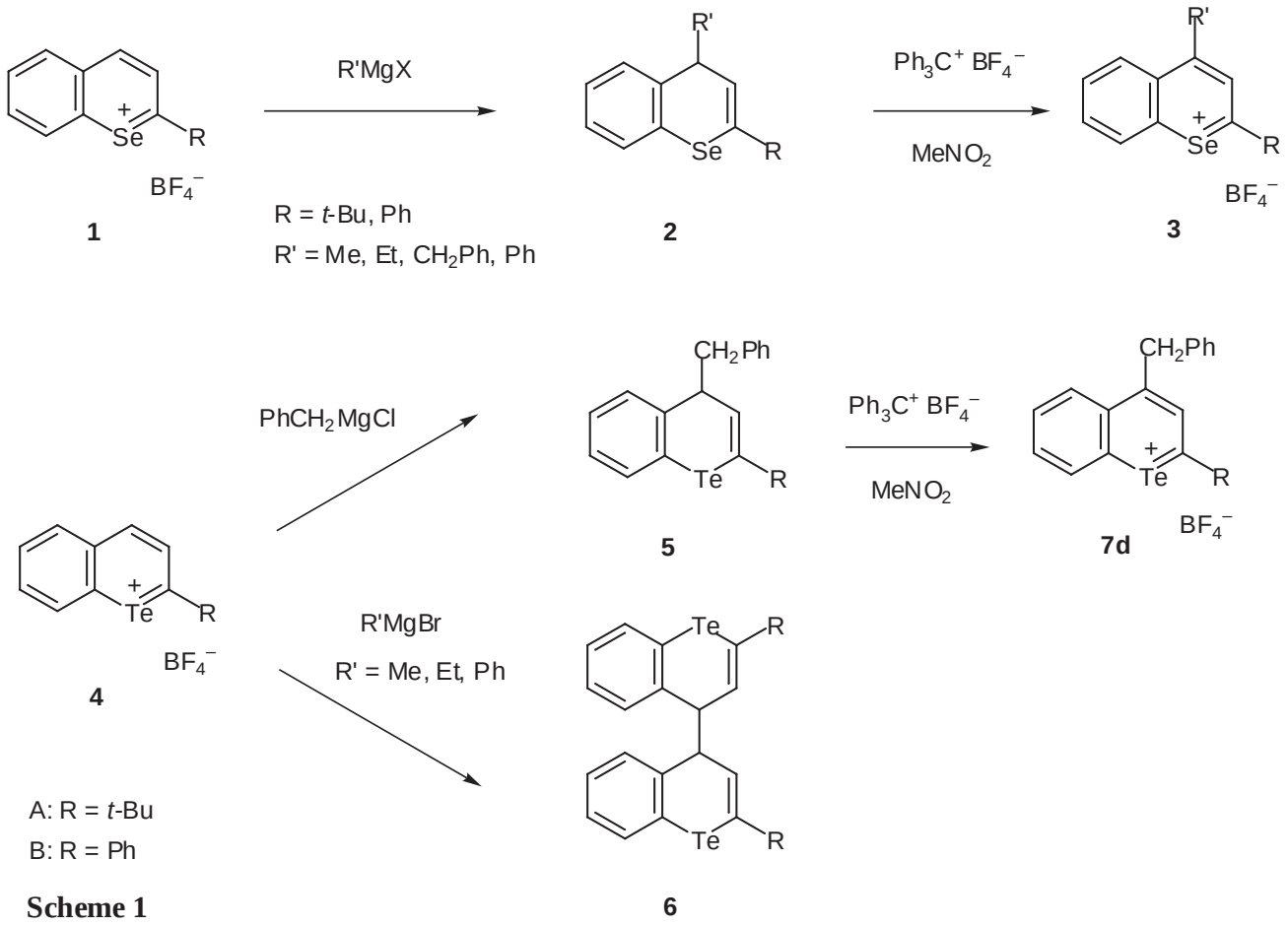
Abstract- The treatment of the 2-*tert*-butyl- (**8A**) and 2-phenyltellurochromen-4-ones (**8B**) with Grignard reagents (MeMgBr, EtMgBr, PhMgBr and $PhCH_2MgCl$) gave the corresponding 4-substituted 4-hydroxy-4*H*-tellurochromenes (**9**) in good yields, respectively. The obtained compounds (**9**) were readily transformed into the 2,4-disubstituted 1-benzotelluropyrylium salts (**7**) by treatment with $Ph_3C^+ BF_4^-$ in acetic acid in high yields. The 4-benzyl-1-benzotelluropyrylium salts (**7Ad**) and (**7Bd**) were also prepared from the 4-benzyl-tellurochromenes (**5**), which were obtained by the reaction of the 1-benzotelluropyrylium salts (**4**) with $PhCH_2MgCl$.

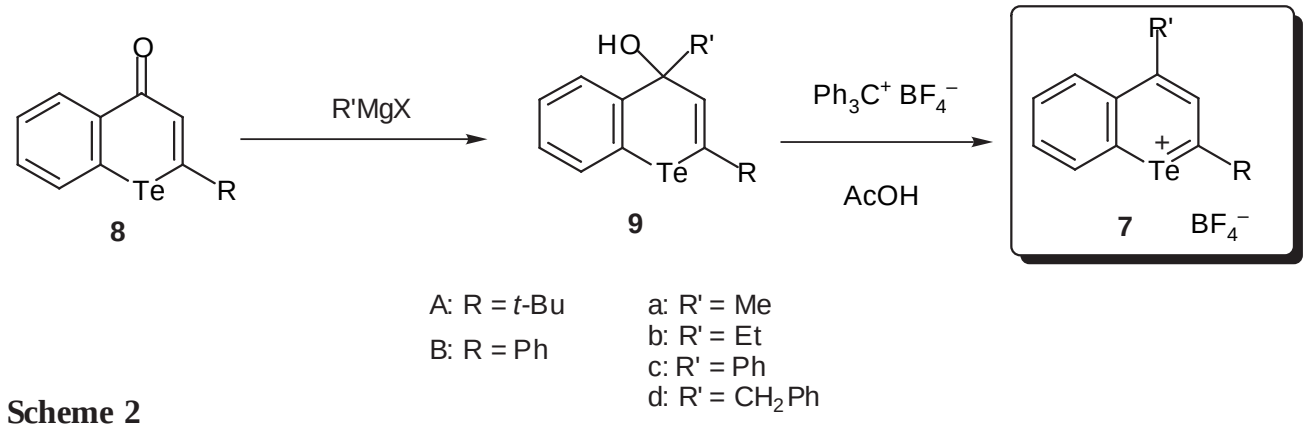
The chemistry of the telluropyrylium compounds,[2] six-membered aromatic heterocycles containing a positively charged tellurium atom, has rapidly developed when comparing them to the thio-[3,4] and selenopyrylium compounds[3,4] during the last twenty years. Detty *et al*. have reported the preparation of several derivatives of monocyclic[5] and benzene ring-fused[6] telluropyrylium salts having a methoxy group on the benzene ring, and described the condensation reactions with carbonyl-containing compounds and other species. The unsubstituted 1-benzotelluropyrylium salt was synthesized as the perchlorate by Nivorozhkin and Sadekov[7] in 1986. However, the simple ring system of the 1-benzotelluropyrylim salts having two carbon functional groups on the pyrylium ring has not been prepared.

Previously, we described the preparation of the 1-benzoselenopyrylium salts (**1**)[8] and the 2-substituted 1-benzotelluropyrylium salts (**4**)[9] from the corresponding selleno- and tellurochromen-4-ones[10] in two steps *via* the selenochromenes or tellurochromenes, respectively. The reactions of the salts (**1**)[11] and (**4**)[9] with a nucleophile have also been reported. More recently, the synthesis of the 2,4-disubstituted 1-



Scheme 1

benzoselenopyrylium salts (**3**)[12] was achieved by the reaction of the 2-substituted 1-benzoselenopyrylium salts (**1**) with the Grignard reagent followed by the treatment of triphenylcarbenium tetrafluoroborate (Ph_3C^+ BF_4^-) *via* the 2,4-disubstituted 4*H*-selenochromenes (**2**). In contrast, the reaction of the telluropyrylium salts (**4**) with benzylmagnesium bromide gave the 4-benzyl-4*H*-tellurochromenes (**5**) as normal coupling products in moderate yields. However, the treatment of **4** with other Grignard reagents, such as the methyl-, ethyl- or phenylmagnesium bromide resulted in



Scheme 2

decomposition of the starting materials to give a complex mixture including a small quantity of the dimeric product (**6**). Although both the 4*H*-selenochromenes[11] and tellurochromenes[9] having a functional group at the C-4 position have been obtained by the reaction of the corresponding pyrylium salts with several nucleophiles, the 4-alkyl or 4-phenyltellurochromenes could not be obtained in this way. Thus, the practical introducing a normal carbon functional group into the C-4 position of the 1-benzotelluropyrylium salts (**4**) failed. Here, we present an easy two-step route to the preparation of the 1-benzotelluropyrylium salts (**7**) having two carbon functional groups at the C-2 and C-4 positions from the corresponding tellurochromen-4-ones (**8**).[10]

The general successful synthesis of the 1-benzotelluropyrylium salts (**7**) having two carbon functional groups at the C-2 and C-4 positions was achieved as shown in Scheme 2. The reaction of **8** with a small excess of methylmagnesium bromide in tetrahydrofuran (THF) at room temperature gave the 4-hydroxy-4-methyl-4*H*-tellurochromenes (**9a**) in good yields. The ethyl-, phenyl- and benzylmagnesium bromide (chloride) also smoothly reacted with the tellurochromen-4-ones (**8**) to afford the corresponding coupling products (**9**) in good yields. These compounds (**9**) were unstable and decomposed during the purification by silica gel chromatography. Thus, **9** were used in the next step after treatment with charcoal in ethanol. Treatment of the 2-*tert*-butyl- (**9A**) and 2-phenyl-4-hydroxytellurochromenes (**9B**) with 1.1 equivalents of Ph_3C^+ BF_4^- in acetic acid at room temperature, followed by the addition of dry ether afforded the desired 1-benzotelluropyrylium tetrafluoroborates (**7A**) and (**7B**) by introduction of the carbon functional group at the C-4 position, in high isolated yields as yellow prisms.

The 4-benzyl-1-benzotelluropyrylium salts (**7Ad**) and (**7Bd**) were also prepared from the 4-benzyltellurochromenes (**5**). **5** were treated with 1.1 equivalents of Ph_3C^+ BF_4^- in nitromethane at room temperature, followed by the addition of dry ether to afford the corresponding 4-benzyltelluropyrylium salts (**7d**) in similar good yields. The 4-phenyltelluropyrylium salts (**7Ac**) and (**7Bc**) are thermally stable but moisture-sensitive, and can be recrystallized from chloroform. Although the 1-benzotelluropyrylium salts (**7Aa**), (**7Ab**), (**7Ad**), (**7Ba**), (**7Bb**) and (**7Bd**) having a primary alkyl group at the C-4 position could be isolated and measured by ^{1}H NMR spectrometry, they gradually decomposed in solution and even during storage in a refrigerator. Thus, the clear ^{13}C NMR spectal data for the methyl, ethyl and benzyl derivatives could not be obtained.

In our previous study, we observed that BF_4^-, the counter anion of the 1-benzyl-2-benzotelluropyrylium salts,[13] abstracted the β–hydrogen of the methylene carbon in the benzyl group to form the 1-benzylidene-isotellurochromenes. Furthermore, the 1-benzoseleno- (**1**)[8] and 1-benzotelluropyrylium salts (**4**)[9] having a primary alkyl group, such as the methyl and *n*-butyl group at the C-2 position, could not be isolated due to their generation of unstable *exo*-methylene compounds by a similar β–hydrogen elimination. In addition, we observed that the reaction of the 4-ethyl-2-*tert*-butyl-1-benzoselenopyrylium salt with a nucleophile resulted in the δ–hydrogen elimination to give the 4-ethylidenetellurochromene.

Table 1 4-Substituted 2-*tert*-butyl-4-hydroxy- (**9A**) and 4-hydroxy- 2-phenyl-4*H*-selenochromenes (**9B**)

9	Appearance Yield (%)	Formula HRMS (Found)	IR ν_{OH} (cm^{-1})	^{1}H NMR (90 MHz, $CDCl_3$) δ, *J* (Hz) OH	3-H	R-H	Ph-H (5-, 6-, 7-, 8-H)	R'-H
9Aa	yellow prisms mp 107-109 °C[a] 80	$C_{14}H_{18}OTe$ 332.0421 (332.0427)	3367 3320	2.5 (br s)	6.18 (s)	1.20 (9H, s) *t*-Bu	7.0-7.9 (4H, m) Ph-H	1.49 (3H,s) Me
9Ba	orange oil 69	$C_{16}H_{14}OTe$ 352.0108 (352.0118)	3390	2.2 (br s)	6.56 (s)		7.1-8.0 (9H, m) Ph-H	1.58 (3H, s) Me
9Ab	red oil 91	$C_{15}H_{20}OTe$ 346.0577 (346.0573)	3400	2.5 (br s)	6.12 (s)	1.21 (9H, s) *t*-Bu	7.0-7.9 (4H, m) Ph-H	0.82, 1.85 (3H, t, *J* = 7, 2H, q, *J* = 7) Et
9Bb	orange oil 82	$C_{17}H_{16}OTe$ 366.0264 (366.0279)	3430	2.3 (br s)	6.50 (s)		7.1-7.9 (9H, m) Ph-H	0.89, 1.90 (3H, t, *J* = 7, 2H, q, *J* = 7) Et
9Ac	orange oil 93	$C_{19}H_{20}OTe$ 394.0578 (394.0578)	3409	2.9 (br s)	6.62 (s)	1.23 (9H, s) *t*-Bu	6.8-7.9 (9H, m)	
9Bc	orange oil 82	$C_{21}H_{16}OTe$ 414.0265 (414.0259)	3400	2.9 (br s)	6.92 (s)		6.9-7.9 (14H, m) Ph-H	
9Ad	red oil 84	$C_{20}H_{22}OTe$ 408.0734 (408.0721)	3400	2.5 (br s)	5.85 (s)	1.17 (9H, s) *t*-Bu	7.0-7.7 (9H, m) Ph-H	2.82, 3.29 (each 1H, d, *J* = 13.4) CH_2Ph
9Bd	red oil 76	$C_{22}H_{18}OTe$ 428.0330 (428.0333)	3420	2.5 (br s)	6.24 (s)		7.0-7.8 (14H, m) Ph-H, CH_2*Ph*	2.90, 3.42 (each 1H, d, *J* = 13.4) CH_2Ph

a: recrystallized from acetone – hexane.

Table 2 Spectral data for the 2,4-disubstituted 1-benzotelluropyrylium salts (**7**)

Compd	IR	^{1}H NMR (400 MHz, CD_3CN) δ, *J* (Hz)			
No	ν BF_4^- (cm^{-1})	3-H	R-H	Ph-H (5-, 6-, 7-, 8-H)	R'-H
7Aa	1054	8.69 (s)	1.66 (9H, s) *t*-Bu	7.93-8.07 (2H, m) 8.51-8.63 (2H, m) Ph-H	2.86 (3H, s) Me
7Ba	1043	8.73 (s)		7.20-7.96 (7H, m) 8.40-8.91 (2H, m) R = Ph, Ph-H	2.94 (3H, s) Me
7Ab	1079	8.84 (s)	1.67 (9H, s) *t*-Bu	7.92-8.10 (2H, m) 8.84-8.89 (2H, m) Ph-H	1.49, 1.95 (3H, t, *J* = 7.6, 2H, q, *J* = 7.6) Et
7Bb	1079	8.90 (s)		7.72-8.10 (7H, m) 8.60-8.93(2H, m) R = Ph, Ph-H	1.32, 1.94 (3H, t, *J* = 7.6, 2H, q, *J* = 7.6) Et
7Ac	1060	8.68 (s)	1.67 (9H, s) *t*-Bu	7.64-7.75 (5H, m), 7.89-7.99 (2H, m) 8.73 (1H, d, J = 8.3), 8.96 (1H, d, J = 7.1) R' = Ph, Ph-H	
7Bc	1065	8.73 (s)		7.63-7.99 (12H, m) 8.73 (1H, d, *J* = 7.6), 8.95 (1H, d, *J* = 6.8) R = R' = Ph, Ph-H	
7Ad	1058	8.82 (s)	1.63 (9H, s) *t*-Bu	7.29-7.60 (5H, m), 7.91-8.01 (2H, m), 8.81-8.92 (1H, m), 9.22-9.23 (1H, m) R' = CH_2*Ph*, Ph-H	4.71 (2H, s) *CH_2*Ph
7Bd	1070	8.91 (s)		7.20-7.47 (12H, m), 8.82-8.92 (1H, m), 9.22-9.33 (1H, m) R = Ph, R' = CH_2*Ph*, Ph-H	4.49 (2H, s) *CH_2*Ph

Based on this information, the instability of the 1-benzotelluropyrylium salts (**7**) having a primary alkyl group at the C-4 position may be reasonable.

In conclusion, the facile two-step preparation of the 1-benzotelluropyrylium salts having two carbon functional groups on the pyrylium ring from the tellurochromen-4-ones was achieved in the present study. The properties associated with the stability of these telluropyrylium salts were elucidated.

EXPERIMENTAL

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Horiba FT-720 spectrophotometer. MS and HRMS were recorded on a JEOL JMS-DX300 instrument. ^{1}H NMR spectra were recorded on a PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in $CDCl_3$ or CD_3CN using TMS as internal standard and *J* values are given in Hz. ^{13}C NMR spectra were recorded on a JEOL JNM-GSX 400 (100 MHz) spectrometer. Microanalyses were performed in the Microanalytical Laboratory of this Faculty.

Reaction of tellurochromen-4-ones (8) with MeMgBr: Formation of 4-hydroxy-4-methyl-4*H*-tellurochromenes (9a)

MeMgBr (1.2 mmol) in ether solution (2 mL) was slowly added to a mixture of the tellurochromen-4-one (**8**, 1 mmol) in THF (5 mL) at rt under an argon atmosphere. The resulting mixture was stirred at rt for 1 h until the disappearance of the starting material, and quenched by the addition of saturated aqueous NH_4Cl solution (10 mL). The resulting mixture was extracted with Et_2O (30 mL x 3). The organic extracts were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo*. The results and spectral data for **9** are summarized in Table 1.

4-Ethyl-4-hydroxy-4*H*-tellurochromenes (9b)

The tellurochromen-4-ones (**1**) were treated with EtMgBr instead of MeMgBr and worked up as described for the preparation of **9a** to give **9b**.

4-Hydroxy-4-phenyl-4*H*-tellurochromenes (9c)

The tellurochromen-4-ones (**1**) were treated with PhMgBr instead of MeMgBr and worked up as described for the preparation of **9a** to give **9c**.

4-Benzyl-4-hydroxy-4*H*-tellurochromenes (9d)

The tellurochromen-4-ones (**1**) were treated with $PhCH_2MgCl$ instead of MeMgBr and worked up as described for the preparation of **9a** to give **9d**.

Preparation of 1-benzotelluropyrylium tetrafluoroborate (7) from 9

Ph_3C^+ BF_4^- (363 mg, 1.1 mmol) was added to a stirred solution of the crude 4-hydroxytellurochromene (**9**, *ca.* 1.0 mmol) in dry AcOH (5.0 mL) and the mixture was stirred at rt for 30 min. To the reaction mixture was added dry Et_2O (*ca*. 100 mL) to precipitate the telluropyrylium salt (**7**). The salt (**7**) was obtained in a nearly pure state, and recrystallized from $CHCl_3$. The spectral data (IR and ^1H NMR) for the salts (**7**) are listed in Table 2.

2-*tert*-Butyl-4-methyl-1-benzotelluropyrylium tetrafluoroborate (7Aa): 88 % yield, yellow prisms, mp 168-171 °C. *Anal.* Calcd for $C_{14}H_{17}BF_4Te$: C, 42.07; H, 4.29. Found: C, 41.80; H, 4.39.

4-Methyl-2-phenyl-1-benzotelluropyrylium tetrafluoroborate (7Ba): 73 % yield, yellow prisms, mp 165-167 °C. *Anal.* Calcd for $C_{16}H_{13}BF_4Te$: C, 45.79; H, 3.12. Found: C, 45.49; H, 3.11.

2-*tert*-Butyl-4-ethyl-1-benzotelluropyrylium tetrafluoroborate (7Ab): 80 % yield, yellow prisms, mp 169-171 °C. *Anal.* Calcd for $C_{15}H_{19}BF_4Te$: C, 43.55; H, 4.63. Found: C, 43.39; H, 4.66.

4-Ethyl-2-phenyl-1-benzotelluropyrylium tetrafluoroborate (7Bb): 81 % yield, yellow prisms, mp 131-133 °C. *Anal.* Calcd for $C_{17}H_{15}BF_4Te$: C, 47.07; H, 3.49. Found: C, 46.97; H, 3.41.

2-*tert*-Butyl-4-phenyl-1-benzotelluropyrylium tetrafluoroborate (7Ac): 89 % yield, yellow prisms, mp 115-118 °C. ^{13}C NMR (CD_3CN): 32.0 (q), 48.5 (s), 130.0 (d), 130.1 (d), 131.2 (d), 132.3 (d), 133.5 (d), 133.7 (s), 136.8 (d), 137.5 (d), 137.6 (d), 142.4 (s), 150.1 (s), 167.0 (s), 221.6 (s). *Anal.* Calcd for $C_{19}H_{19}BF_4Te$: C, 49.42; H, 4.15. Found: C, 49.41; H, 4.21.

2,4-Diphenyl-1-benzotelluropyrylium tetrafluoroborate (7Bc): 83 % yield, yellow prisms, mp 128-131 °C. ^{13}C NMR (CD_3CN): 129.5 (d), 130.0 (d), 130.3 (d), 131.3 (d), 131.6 (d), 132.6 (d), 133.4 (d), 133.9 (s), 135.3 (d), 136.5 (d), 137.4 (d), 138.1 (d), 142.3 (s), 143.2 (s), 150.9 (s), 167.2 (s), 198.0 (s). *Anal.* Calcd for $C_{21}H_{15}BF_4Te$: C, 52.32; H, 3.36. Found: C, 52.36; H, 3.14.

4-Benzyl-2-*tert*-butyl-1-benzotelluropyrylium tetrafluoroborate (7Ad): 78 % yield, yellow prisms, mp 148-150 °C. *Anal.* Calcd for $C_{20}H_{21}BF_4Te$: C, 50.49; H, 4.45. Found: C, 50.29; H, 4.40.

4-Benzyl-2-phenyl-1-benzotelluropyrylium tetrafluoroborate (7Bd): 73 % yield, yellow prisms, mp 135-137 °C. *Anal.* Calcd for $C_{22}H_{17}BF_4Te$: C, 53.30; H, 3.46. Found: C, 53.19; H, 3.33.

Preparation of 7d from 5

4-Benzyltellurochromenes (**5**) were treated with Ph_3C^+ BF_4^- in $MeNO_2$ instead of AcOH and worked up as described for the preparation of **7** from **9** to give **7** from **5**.

7Ad: 91 % yield.

7Bd: 86 % yield.

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