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PERKIN 1 COMMUNICATION

Studies on tellurium-containing heterocycles. Part 10.[1] 2-Benzotelluropyrylium salts: first preparation and reactions with Grignard reagents

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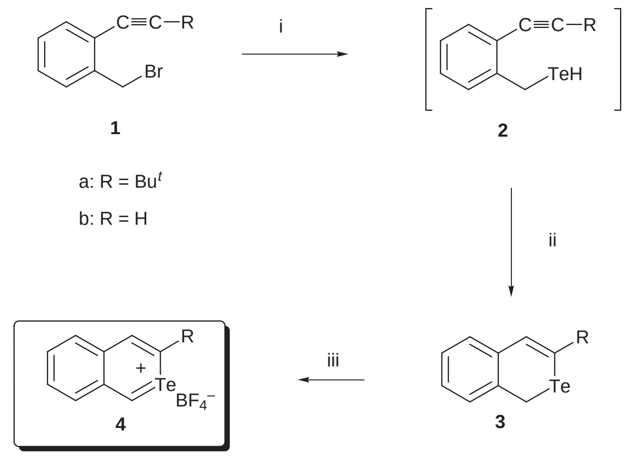
The first simple preparation of 2-benzotelluropyrylium salts 4 from *o*-ethynylbenzyl bromides 1 in two steps, and the characteristic reaction of these salts 4 with benzylmagnesium bromide and other Grignard reagents are described.

The chemistry (structure and physical properties, syntheses and reactions) of not only the pyrylium salts[2] but also the thiopyrylium salts[3] has been widely investigated and is now well established. Recently, extensive synthetic studies on their selenium[4] and tellurium[5] analogs have been undertaken, however the title compounds, the 2-benzotelluropyrylium salts, have not been prepared until now. We have previously focused on the synthesis of various tellurium- or selenium-containing heterocycles[6] by an intramolecular cyclization of the tellurol or selenol moieties to an ethynyl group. In our continuing studies, we herein describe the successful synthesis of the 2-benzotelluropyrylium salts and their reactions with Grignard reagents.



Scheme 1 *Reagents and conditions*: i, NaHTe (1.2 equiv.), DMF, 0 °C, 1 h; ii, EtOH, 90 °C, 1–3 h; iii, Ph_3C^+ BF_4^- (1 equiv.), $MeNO_2$, room temp., 30 min

The synthesis of the 2-benzotelluropyrylium salts **4** is shown in Scheme 1. In order to obtain isotellurochromenes **3**, the precursors for the preparation of the telluropyrylium salts **4**, the conversion from *o*-ethynylbenzyl bromides **1** to the telluroles **2** was examined. Treatment of the benzyl bromides **1** with sodium hydrogen telluride[7] in DMF at 0 °C, followed by addition of EtOH, and then heating at 90 °C, resulted in a direct ring closure to afford isotellurochromenes **3** (**3a**: 84% yield, **3b**: 64% yield) *via* the benzyltellurol intermediates **2**.[†] The isotellurochromenes **3** were produced by the 6-*endo-dig* ring closure of **2** at the sp carbon atom of the acetylenic moiety. The 5-*exo-dig* reaction products were not obtained. The isochromenes **3** were treated with triphenylcarbenium tetrafluoroboranuide (Ph_3C^+ BF_4^-) in $MeNO_2$ at room temperature to give the desired 2-benzotelluropyrylium tetrafluoroboranuides **4** (**4a**: 94% yield, **4b**: 89% yield) as stable pale green prisms. The salts **4** are the first synthetic examples of 2-benzotelluropyrylium salts. As expected, **4** have high reactivities and are easily decomposed on contact with water or alcohol. Thus, in order to examine the chemical behavior of the novel telluropyrylium salts **4** towards nucleophiles, the reaction of **4** with some Grignard reagents was carried out. Contrary to our expectations, treatment of the salts **4** with Grignard reagents, such as methyl-, ethyl- or phenyl-magnesium bromide (iodide) in THF at 0 °C resulted in a self-coupling reaction at the C-1 position to give 1,1′-bis(isotellurochromenyl) **5** as the sole characterized product in moderate yield (Scheme 2). However, when benzylmagnesium bromide was used as the Grignard reagent in Et_2O at 0 °C, 1-benzylisotellurochromenes **6** (**6a**: 48% yield, **6b**: 21% yield), normal coupling products, were obtained. In this case, no dimers **5** were obtained. It is already known that the reaction of telluraxanthylium salts[8] with reducing agents, such as zinc powder or with nucleophiles, such as ammonium chloride, affords the telluraxanthyl dimers, produced *via* a free radical mechanism. This result clearly supports the present formation of **5** proceeding *via* a similar radical mechanism. In contrast, a similar reaction of their selenium analogs, the 2-benzoselenopyrylium salts, with any Grignard reagent gave the normal corresponding 1-substituted isoselenochromenes in good yields.

In addition, treatment of 1-benzyl-3-*tert*-butylisotellurochromene **6a** with Ph_3C^+ BF_4^- gave 1-benzyltelluropyrylium tetrafluoroboranuide **7a** as the sole product. The ^1H NMR spectrum of the crude isolated telluropyrylium salt **7a** in CD_3CN showed two *tert*-butyl signals at δ 1.59 and 1.29 in a ratio of 2:3, indicating the presence of the salt **7a** and the benzylidene compound **8a**. Treatment of the salt **7a** with base or by alumina column chromatography using methylene chloride as the eluent quantitatively gave **8a**. This finding suggests that the telluropyrylium salt **7a** exists in the solvent as an equilibrium mixture of **7a** and **8a**. The stereochemistry of the olefin moiety in **8a** was determined by a nuclear Overhauser enhancement (NOE) measurement. A NOE was observed between the benzylidene 1′-H and the aromatic 8-H in the 400 MHz ^1H NMR spectrum of **8a**. Thus, the olefin moiety was determined to have (*Z*)-stereochemistry. In the case of a similar treatment of the 3-unsubstituted isotellurochromenes **6b** with Ph_3C^+ BF_4^-, the formation of salt **7b** and the benzylidene compound **8b** was confirmed by the ^1H NMR spectrum in CD_3NO_2. However, both **7b** and **8b** were too unstable to isolate. The proposed mechanism for the formation of **8** is shown in Scheme 2.

[†] The formation of compounds **2** was characterized by the isolation of bis(*o*-ethynylbenzyl) ditellurides, which were obtained by potassium ferricyanide oxidation of **2** before heating in ethanol.

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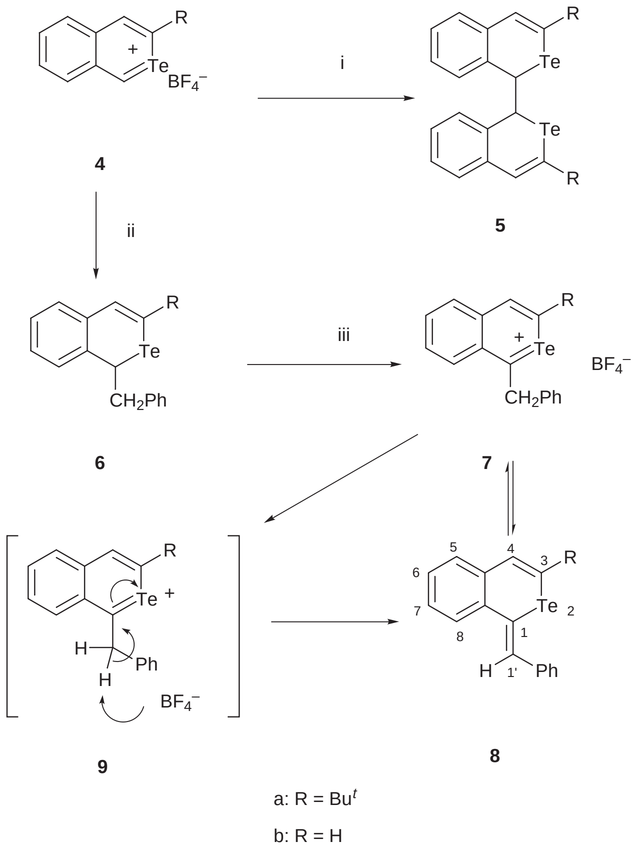

Scheme 2 *Reagents and conditions*: i, EtMgBr (MeMgI, PhMgBr), THF, 0 °C, 30 min; ii, $PhCH_2MgBr$, Et_2O, 0 °C, 30 min; iii, Ph_3C^+ BF_4^- (1 equiv.), $MeNO_2$, room temp., 2 h

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 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.

Isotellurochromene 3a

A solution of *o*-ethynylbenzyl bromide **1** (2.51 g, 10 mmol) in DMF (10 ml) was slowly added to a solution of sodium hydrogen telluride (12 mmol), which was freshly prepared from tellurium dust (1.53 g) and sodium borohydride (0.54 g) in DMF (40 ml) at 0 °C under an argon atmosphere. The reaction mixture was stirred under the conditions for 1 h. Ethanol (40 ml) was added to the reaction mixture, and then the whole mixture was heated at 90 °C with stirring for 1–3 h. After addition of water, the aqueous mixture was extracted with benzene. The organic extracts were washed with water and brine, dried ($MgSO_4$) and evaporated. The resulting residue was chromatographed on silica gel using *n*-hexane as eluent to give pure **3a**, yellow prisms, mp 63 °C (from *n*-hexane); δ_H($CDCl_3$, 90 MHz) 1.29 (9H, s, Bu^t), 3.79 (2H, s, 1-H_2), 6.64 (1H, s, 4-H), 7.10–7.26 (4H, m, Ar-H) (HRMS *m*/*z* Calc. for $C_{13}H_{16}Te$: 302.0315. Found: 302.0313).

2-Benzotelluropyrylium salt 4a

Ph_3C^+ BF_4^- (1.88 g, 5.5 mmol) was added to a stirred solution of the isochromene **3a** (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 to precipitate the telluropyrylium salt **4a**, pale green prisms, mp 101 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1054 (BF_4^-); δ_H(CD_3CN, 400 MHz) 1.68 (9H, s, Bu^t), Ph-H [8.00 (1H, ddd, *J* 8.8, 7.2, 1.5), 8.34 (1H, br d, *J* 8.4), 8.47 (1H, ddd, *J* 8.4, 7.2, 1.5), 8.49 (1H, br d, *J* 8.8)], 9.14 (1H, s, 4-H), 13.22 (1H, s, 1-H); δ_C(CD_3CN, 100 MHz) 33.34 (q), 43.80 (s), 131.42 (d), 132.07 (d), 135.40 (d), 137.84 (d), 139.05 (d), 139.85 (s), 143.69 (s), 182.85 (s), 188.83 (s) (Anal. Calc. for $C_{13}H_{15}BF_4Te$: C, 40.49; H, 3.93. Found: C, 40.35; H, 3.75%).

1-Benzylisotellurochromene 6a

A solution of $PhCH_2MgBr$ (4 mmol) in Et_2O (4 ml) was added to a suspended mixture of telluropyrylium salt **4a** (3 mmol) in Et_2O (10 ml) and the mixture was stirred at room temperature for 30 min. The reaction mixture was quenched by the addition of aqueous NH_4Cl, and extracted with Et_2O. The ethereal fractions were washed with brine, dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel using hexane–CH_2Cl_2 (20 : 1) as eluent to give **6a**, yellow oil; δ_H($CDCl_3$, 90 MHz) 1.31 (9H, s, Bu^t), 3.21 (2H, d, *J* 7.1, C*H*$_2$Ph), 3.96 (1H, br t, *J* 7.1, 1-H), 6.78 (1H, s, 4-H), 6.86–7.26 (9H, m, Ar-H); HRMS *m*/*z* Calc. for $C_{20}H_{22}Te$: 392.0785. Found: C, 392.0781.

Selected data for the telluropyrylium salt 7a. Yield 71%, pale green prisms, mp 105–108 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1052 (BF_4^-); δ_H(CD_3CN, 90 MHz) 1.55 (9H, s, Bu^t), 4.82 (2H, s, C*H*$_2$Ph), 7.22–7.59 (9H, m, Ph-H), 8.92 (1H, s, 4-H) (Anal. Calc. for $C_{20}H_{21}BF_4Te$: C, 50.49; H, 4.45. Found: C, 50.64; H, 4.47%).

Selected data for the benzylidene compound 8a. Yellow oil; δ_H($CDCl_3$, 400 MHz) 1.24 (9H, s, Bu^t), 6.86 (1H, s, 4-H), 7.18–7.45 (8H, m, Ph-H), 7.48 (1H, s, 1′-H), 7.53 (1H, br d, *J* 7.8, 8-H); HRMS *m*/*z* Calc. for $C_{20}H_{20}Te$: 390.0628. Found: 390.0627.

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