3-Benzotellurepines: The First Examples of Tellurepines

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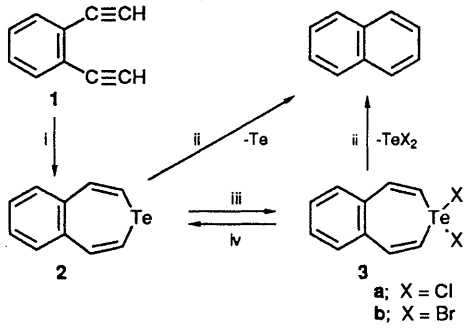
Reaction of *o*-diethynylbenzene with sodium telluride in the presence of hydrazine hydrate gives 3-benzotellurepine **2**, which is converted into the 3,3-dihalogeno derivatives **3** by treatment with sulphuryl chloride or bromine; these compounds are the first examples of tellurepines.

The synthesis of fully unsaturated seven-membered heterocyclic rings (heteroepines) has received increasingly intensive study and a variety of new heteroepine ring systems containing nitrogen,[1a,c] oxygen,[1b,c] phosphorus[2] or boron[3,4] have been prepared. However, heteroepines containing heavier elements are unknown except for stannepines.[3,5] We report here the synthesis of 3-benzotellurepines, the first examples of tellurium-containing heteroepines; five-membered tellurophenes are known however.[6]

o-Diethynylbenzene **1**[7] was treated with sodium telluride in the presence of hydrazine hydrate in benzene–water containing methyltrioctylammonium chloride as a phase-transfer catalyst at room temperature to give the desired 3-benzotellurepine **2** in 60–70% yield as a yellow oil.† The tellurepine **2** is relatively unstable and gradually decomposes to naphthalene and tellurium; decomposition is almost complete after 2–3 days in solution at room temperature. This behaviour is analogous to that of borepines[3,4] and 3-benzophosphepines,[2] which decompose to benzene and napthalene, respectively.



Scheme 1 *Reagents and conditions*: i, Na_2Te, $Me(octyl)_3N^+Cl^-$, $H_2NNH_2{\cdot}H_2O$, benzene–H_2O, room temp., 6 h; ii, room temp. or heat; iii, SO_2Cl_2 or Br_2, hexane, 0 °C, 10–20 min; iv, Na_2S, hexane–H_2O, room temp., 30 min

In the absence of hydrazine hydrate, this reaction did not occur, indicating that such a reducing agent is essential.‡ Therefore, the formation of **2** from **1** may proceed by a radical-anion-chain mechanism initiated by electron transfer from the reducing agent to the ethynyl group, by analogy with the reaction of ethynylbenzene with tellurium.[8]

Treatment of **2** with sulphuryl chloride in hexane gave the 3,3-dichloro compound **3a** [m.p. 45–48 °C (decomp.), yield 50–60%†] and treatment with bromine afforded the 3,3-dibromo compound **3b** [m.p. 67–70 °C (decomp.), yield 70%†]. The halogeno compounds **3** are somewhat more stable than **2**, and reverted to **2** on treatment with sodium sulphide in hexane–water.

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† Satisfactory elemental analyses and mass spectral data were obtained for all new compounds reported. The ^1H and ^{13}C NMR spectral data for the alkene parts of **2** and **3** are reasonable compared with those for 3-benzostannepines[3] and phenyl vinyl telluride (T. Kauffmann and H. Ahler, *Chem. Ber.*, 1983, **116**, 1001). Compound **2**: ^1H NMR ($CDCl_3$) δ 6.75 (2H, d, *J* 10.3 Hz, 2- and 4-H), 7.58 (2H, d, *J* 10.5 Hz, 1- and 5-H) and 7.16–7.25 (4H, m, Ph-H); ^{13}C NMR ($CDCl_3$) δ 106.26 (2C, d, 2- and 4-C), 142.02 (2C, d, 1- and 5-C) and C(Ph) [126.51 (2C, d), 130.90 (2C, d) and 139.95 (2C, s)]; **3a**: ^1H NMR δ 6.64 (2H, d, *J* 10.5 Hz, 2- and 4-H), 7.25–7.35 (4H, m, Ph-H) and 7.79 (2H, d, *J* 10.5 Hz, 1- and 5-H); **3b** ^1H NMR δ 6.77 (2H, d, *J* 10.4 Hz, 2- and 4-H), 7.30–7.35 (4H, m, Ph-H) and 7.75 (2H, d, *J* 10.4 Hz, 1- and 5-H).

‡ Commercially available sodium telluride (CERAC Inc., Wisconsin, USA) was used. The tellurepine **2** was also obtained by treatment of **1** in benzene with a sodium telluride-forming reaction mixture (Te, NaOH, $NH_2NH_2{\cdot}H_2O$, H_2O, 60 °C, 5 h)[8] in the presence of methyltrioctylammonium chloride at room temperature.