

SYNTHESIS OF 2,7-DIHYDRO-3,4-5,6-DIBENZOTELLUREPIN— A NEW HETEROCYCLIC COMPOUND

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Abstract—The reaction of 2,2-bis(bromomethyl)biphenyl with tellurium powder and sodium iodide gave the orange compound 1,1-diiodo-2,7-dihydro-3,4-5,6-dibenzotellurepin (1), which is easily reduced with hydrazine hydrate to 2,7-dihydro-3,4-5,6-dibenzotellurepin (2). The latter compound readily forms a black-brown 1:1 complex with TCNQ. The former could be converted to its 1,1-bis(diethylthiocarbamate)-2,7-dihydro-3,4-5,6-dibenzotellurepin (3) and 1-phenyl-2,7-dihydro-3,4-5,6-dibenzotellurepinium tetraphenylborate (4), respectively, by treatment with $\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2$ and $\text{NaB}(\text{C}_6\text{H}_5)_4$. The UV-vis, IR, ESR and ^1H NMR spectral data for the new compounds are presented and discussed.

The chemistry of heterocyclic tellurium compounds, in which tellurium is a part of a five- or six-membered ring system, is extensive and well studied.¹ In contrast, little is known about telluracycloheptane. The first example was a steriodal telluracycloheptane which was prepared in 1972 from the reaction of a steriodal methane-sulphonate with sodium telluride.²

Recently, Sashida *et al.*³ reported the synthesis of 3H-3-benzotellurepin by reacting *o*-diethynylbenzene with tellurium powder, hydrazine and NaOH. So far we have been interested in the synthesis of heterocyclic tellurium compounds⁴ and their use as ligands with rhodium(III) and rhodium(I) ions⁵ or as donors in charge-transfer complexes.⁶

Now we report the synthesis and reaction of 2,7-dihydro-3,4-5,6-dibenzotellurepin, a hitherto unknown tellurium seven-membered ring compound, and its derivatives. It is worth noting that the corresponding selenium analogues have long been known.⁷

EXPERIMENTAL

Physical measurements

IR spectra were obtained using a Pye-Unicam SP3-300s instrument. All melting points were determined by a Gallenkamp melting point apparatus

and are uncorrected. Measurements of UV-vis spectra in CH_2Cl_2 solution were performed with a Pye-Unicam SP8-100 spectrophotometer. ^1H NMR spectra were determined with a Jeol EX-90 instrument using TMS as an internal standard. Elemental analyses were obtained on a Perkin-Elmer 240 Elemental Analyser instrument. An ESR spectrum was obtained at room temperature with a Varian E-109 spectrometer.

Conductivity measurements

These were determined by DC methods at room temperature. A sample of the $[\text{C}_{14}\text{H}_{12}\text{Te}]^+ [\text{TCNQ}]^-$ complex was compressed into a disc of 10 mm diameter and 2 mm thickness. Two nickel electrodes were deposited on the disc by evaporation *in vacuo* (10^{-7} torr). Copper wires were attached by silver paint.

Synthesis

1,1-Diiodo-2,7-dihydro-3,4-5,6-dibenzotellurepin (1). A mixture of 2,2-bis(bromomethyl)biphenyl (1.7 g, 5 mmol), sodium iodide (3.0 g, 20 mmol) and tellurium powder (0.64 g, 5 mmol) in 2-butoxyethanol (80 cm^3) was stirred with gentle boiling for 6 h. After cooling the reaction mixture deionized water (200 cm^3) was added to cause additional precipitation. The precipitate was filtered off, washed with water and dried. The product was recrystallized from 2-butoxyethanol to give an orange-red

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crystalline solid; m.p. 222°C. $^1\text{H NMR}$: $\delta(\text{CDCl}_3)$ 3.78 (Te—CH₂, q, 4H, $J = 12.2$ Hz) and 7.10–7.41 (Ar—H, m, 8H). Found: C, 29.4; H, 1.9. Calc. for C₁₄H₁₂TeI₂: C, 29.9; H, 2.1%.

2,7-Dihydro-3,4-5,6-dibenzotellurepin (2). Hydrazine hydrate was added to a boiling ethanolic solution of C₁₄H₁₂TeI₂ (1.12 g, 2 mmol) until the orange colour had disappeared. The solution was filtered, then poured into water (200 cm³) and extracted into diethyl ether. The ethereal layer was separated, dried over anhydrous CaCl₂ and taken to dryness on a rotatory evaporator. The resulting yellow powder, on treatment with charcoal and ether, gave yellow crystals; m.p. 87–89°C in 68% yield or 0.41 g. $^1\text{H NMR}$: $\delta(\text{DMSO-d}_6)$ 4.25 (Te—CH₂, q, 4H, $J = 12.6$ Hz) and 7.12–7.50 (Ar—H, m, 8H). Found: C, 54.2; H, 4.4. Calc. for C₁₄H₁₂Te: C, 54.6; H, 3.9%.

1,1-Bis(diethyldithiocarbamato)-2,7-dihydro-3,4-5,6-dibenzotellurepin (3). To a solution of C₁₄H₁₂TeI₂ (2.24 g, 4 mmol) in dichloromethane (30 cm³) was added with stirring a solution of sodium diethyldithiocarbamate (1.5 g, 9 mmol) in absolute ethanol (30 cm³) at room temperature. The residue was treated with dichloromethane (30 cm³) and filtered to remove sodium iodide. Removal of dichloromethane and recrystallization from methanol gave the pale yellow crystals; m.p. 107°C in 76% yield or 1.8 g. $^1\text{H NMR}$: $\delta(\text{CDCl}_3)$ 1.20 (CH₃, t, 12H), 4.05 (CH₂, q, 8H), 4.15 (Te—CH₂, q, 4H, $J = 11.7$ Hz) and 7.18–7.43 (Ar—H, m, 8H). Found: C, 47.5; H, 5.3; N, 4.3. Calc. for C₂₄H₃₂N₂S₄Te: C, 47.7; H, 5.3; N, 4.6%.

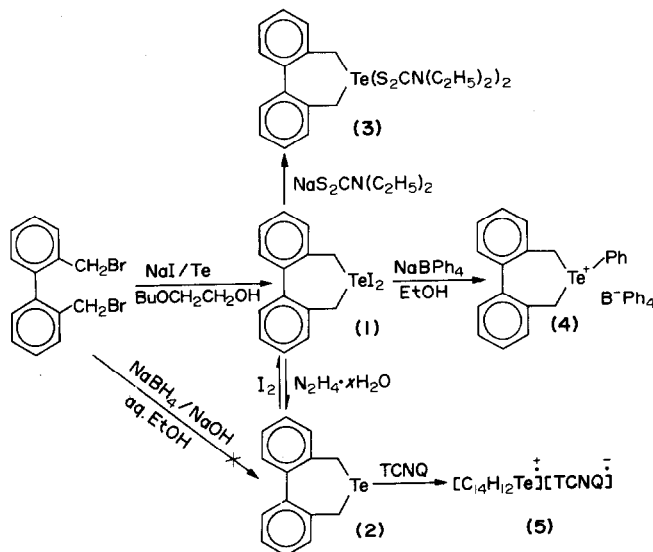
1-Phenyl-2,7-dihydro-3,4-5,6-dibenzotellurepinium tetraphenylborate (4). A mixture of C₁₄H₁₂TeI₂

(1.12 g, 2 mmol) in dry ethanol (100 cm³) was heated to reflux with stirring for 4 h. The solution was filtered hot and white crystals of C₁₄H₁₂Te(Ph)BPh₄ collected in quantitative yield. The product was washed with water and methanol and recrystallized from water/DMF; m.p. 158–160°C. $^1\text{H NMR}$: $\delta(\text{DMSO-d}_6)$ 3.61–4.40 (Te—CH₂, m, 4H), 6.74–7.08 (Ar—H, m, 20H), 7.12–7.40 (Ar—H, m, 4H) and 7.40–7.62 (Ar—H, m, 5H). Found: C, 75.0; H, 4.8. Calc. for C₄₄H₃₇BTe: C, 75.0; H, 5.3%.

Complex of 2,7-dihydro-3,4-5,6-dibenzotellurepin with TCNQ (5). To a solution of 2,7-dihydro-3,4-5,6-dibenzotellurepin (0.31 g, 1 mmol) in acetonitrile (20 cm³) was added a solution of 7,7,8,8-tetracyanoquinodimethane, TCNQ (0.21 g, 1 mmol), in acetonitrile (30 cm³). The resulting solution was stirred under reflux for 3 h, after which the volume of the solution was reduced to 10 cm³ and the residue was left to crystallize. Black-brown crystals were obtained; m.p. 220°C (dec.). Found: C, 60.4; H, 3.1; N, 10.5. Calc. for C₂₆H₁₆N₄Te: C, 61.0; H, 3.1; N, 10.9%.

RESULTS AND DISCUSSION

2,7-Dihydro-3,4-5,6-dibenzotellurepin (2) is formed in 68% yield from the reduction of readily accessible 1,1-diiodo-2,7-dihydro-3,4-5,6-dibenzotellurepin, which in turn can be prepared directly from the reaction of 2,2-bis(bromomethyl)biphenyl with tellurium powder and sodium iodide⁸ (Scheme 1). Attempts to prepare the telluride [i.e. C₁₄H₁₂Te (2)] by reacting 2,2-bis(bromomethyl)biphenyl with sodium telluride⁸ were unsuccessful. This may be due to the thermal instability of the dibenzo-



Scheme 1.

tellurepin ring system at the temperature required for the reaction. $C_{14}H_{12}Te$ (**2**) is soluble in common organic solvents and quite stable at room temperature but it slowly deposited elemental tellurium upon standing in organic solvents (e.g. $CHCl_3$ and alcohols). It forms a 1:1 charge-transfer complex (**5**) with TCNQ (Scheme 1).

The diiodide ($C_{14}H_{12}TeI_2$, **1**) reacts with sodium diethyldithiocarbamate and sodium tetraphenylborate, respectively, to afford compounds **3** and **4** (Scheme 1). Furthermore, the diiodide (**1**) can be prepared by the reaction of the telluride (**2**) with iodine in diethyl ether (Scheme 1).

The IR spectra of all the compounds show two bands between 480 and 525 cm^{-1} due to $\nu_{as}(C-Te)$ and $\nu_s(C-Te)$, which agrees well with previous work.^{8,9} Compound **3**, $C_{14}H_{12}Te(S_2CN(C_2H_5)_2)_2$, shows the characteristic frequencies of diethyldithiocarbamate ligands; its IR spectrum shows $\nu(CN)$ at 1485 cm^{-1} and $\nu(CS)$ at 1000 cm^{-1} as strong bands. Thus, it may be concluded that diethyldithiocarbamate is acting as an unsymmetrical bidentate ligand, as reported by other workers.^{10,11} Complex **5** shows the $\nu(C\equiv N)$ stretching vibration at 2180 cm^{-1} , typical of $TCNQ^{\cdot-}$, suggesting the radical-ion character of this complex.¹²

The electronic spectrum of complex **5** merits special mention; it exhibits an absorption charge-transfer band at 623 nm. Furthermore, the solid-state ESR data showed a sharp and strong signal with a g factor of 2.0025 (± 0.0003). This value is almost the same as those reported for some other telluride-TSNQ complexes^{13,14} and very close to the free-electron value, suggesting that the signal arises from unpaired electron density on TCNQ. However, the electrical conductivity of this complex was semi-conducting ($5.4 \times 10^{-9} \Omega^{-1} cm^{-1}$), suggesting a mixed stacking of donor and acceptor in crystal structures.¹⁵

In the 1H NMR spectra the expected ratios of aliphatic to aromatic protons were observed. The methylene protons (2 and 7) appeared as two doublets of a simple AB pattern. The formation of telluronium salts (i.e. compound **4**) changes the methylene protons to a more complex pattern. The cation phenyl-proton multiplets are downfield from the anion phenyl-proton multiplets (see Exper-

imental), consistent with the large deshielding effect expected in the cation.^{4a}

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