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Synthesis of 1,3-benzotellurazole derivatives from phenyl ureas and tellurium tetrachloride

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ABSTRACT

A method has been developed to prepare previously inaccessible substituted 1,3-benzotellurazoles following an efficient two-step process, consisting of the tellurination of electron rich phenyl ureas with tellurium tetrachloride and subsequent ring closure of the resulting aryl tellurium trichlorides. Tellurination occurs regiospecifically ortho to the urea moiety due to intramolecular Te-O coordination, producing highly crystalline solids that are readily isolated in yields up to 83 %. Subsequent ring closure, accomplished by heating with phosphorus trichloride and subsequent reduction with hydrazine hydrate, provides access to 1,3-benzotellurazole derivatives. Selected products were characterized by X-ray crystallography.

1. Introduction

1,3-Benzotellurazoles are highly stable towards light, air and heat [1,2]. This has fostered interest in developing improved synthetic access and practical applications for these compounds. Initially investigated as photographic anti-fogging agents [3], 1,3-benzotellurazoles have been noted for their tendency to form supramolecular assemblies characterized by the presence of chalcogen bonding interactions [4-6]. Remarkably, these can be stable enough to persist even in the gas phase [7]. Recent work also investigates their photochemical properties [8-10]. Published methods of access to 1,3-benzotellurazoles consist of the reductive cyclization of diaryl ditellurides or aryltellurium halides bearing amide moieties in ortho position with hypophosphorus acid [11] or sodium borohydride [3,12]. Alternatively, these compounds can be prepared by the cyclization of N-[(2-alkyltelluranyl)aryl]benzamides with thionyl chloride [13] or phosphorus oxychloride [9,14]. All methods place significant limitations on the types and locations of substituents that can be present. The required bis(2-aminophenyl) ditelluride derivatives are prepared either from mercurated phenyl amides via Hg-Te exchange [12] or from 2-haloanilines by nucleophilic tellurination with sodium telluride [11]. In addition to employing highly toxic organomercury intermediates, the former method requires blockage of the para position to achieve ortho mercuration while the latter only tolerates a very narrow range of substituents.

Ongoing efforts aim at developing more flexible methods for the preparation of 1,3-benzotellurazoles from easily accessible precursors. The strategy investigated here consists of the tellurination of electron rich aromatics carrying substituents capable of coordinating the incoming tellurium to achieve regiospecific ortho tellurination (Scheme 1). Amides, carbamates, ureas and thioureas were investigated as candidates for the coordinating moiety. There is precedent for this approach, as azobenzene can be selectively ortho tellurated to 2-phenylazophenyltellurium trichloride as a result of Te-N coordination [15]. Similarly, regiospecific C−H bond activation ortho to a dimethylurea moiety was employed for the preparation of substituted biaryl derivatives [16]. A related approach exploits Te-N coordination to selectively ortho-nitrate aromatic tellurium compounds [17]. Surprisingly, little work has been done since to further explore the scope and potential of coordination assisted regiospecific ortho tellurination. The products it furnishes are valuable intermediates in the preparation of five-, six-and seven-membered organotellurium heterocycles [2,18-21].

2. Experimental section

A screening of potential electrophilic tellurination reactions found that 1-phenyl-3,3-dimethylurea derivatives react smoothly with

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tellurium tetrachloride to generate 1-[2-(trichloro- λ^4-tellanyl)phenyl] 3,3-dimethylurea derivatives. Subsequent cyclization furnished the targeted 1,3-benzotellurazoles. The products prepared in this study are summarized in Table 1. Isolated yields listed for ureas **1a-5a** are based on tellurium tetrachloride. Yields for tellurazoles **1b-5b** are based on ureas **1a-5a**.

Caution: Due to the use of toxic phosphorus halides and the possibility of releasing volatile organotellurium byproducts, all reactions should be carried out under a well vented hood.

2.1. Materials and methods

All urea precursors were prepared by reacting the corresponding anilines with dimethylcarbamoyl chloride in the presence of pyridine, following a minor modification of a published procedure [22]: dichloromethane was replaced by tetrahydrofuran as solvent and the 4-dimethylaminopyridine catalyst was omitted because it was found to be unnecessary. All products were recrystallized from toluene before use. 2,3-Dihydro-1,4-benzodioxin-6-amine was prepared as previously published [23]. All other chemicals were purchased as reagent grade and used as received. Silica gel, 40-65 μm, obtained from VWR, was used for flash chromatography. Melting points were recorded in open capillaries using an electrothermal SRS MPA160 apparatus. ^{1}H and ^{13}C nuclear magnetic resonance spectra were collected on a Varian MR400 MHz NMR spectrometer. ^{125}Te nuclear magnetic resonance spectra were collected on a Bruker Avance III HD Nanobay spectrometer. High resolution mass spectra were recorded on a Waters Synapt XS platform. **1a-5a** were recorded in negative mode, the remaining samples in positive mode. $[M\text{-}H]^-$ and $[M+H]^+$ clusters exceeding 15 % of base are listed. Infrared spectra were recorded for pure solids with a Cary 630 FTIR spectrometer. Crystallographic data for **3a** and **1b** were collected at 100 K on a Bruker APEX-II DUO CCD diffractometer using Mo-Kα radiation. Absorption corrections were by the multi-scan method using the APEX3 [24] and the structure was refined against F2 by full-matrix least squares using SHELXL [25]. Anisotropic displacement parameters were employed for the non-hydrogen atoms. Hydrogen atoms were visible in difference maps and were placed in calculated positions and treated as riding in the refinement. C, H, N elemental analyses were performed at Atlantic Microlab, Inc. using a Carlo Erba 1108 automatic analyzer.

2.2. Tellurium tetrachloride

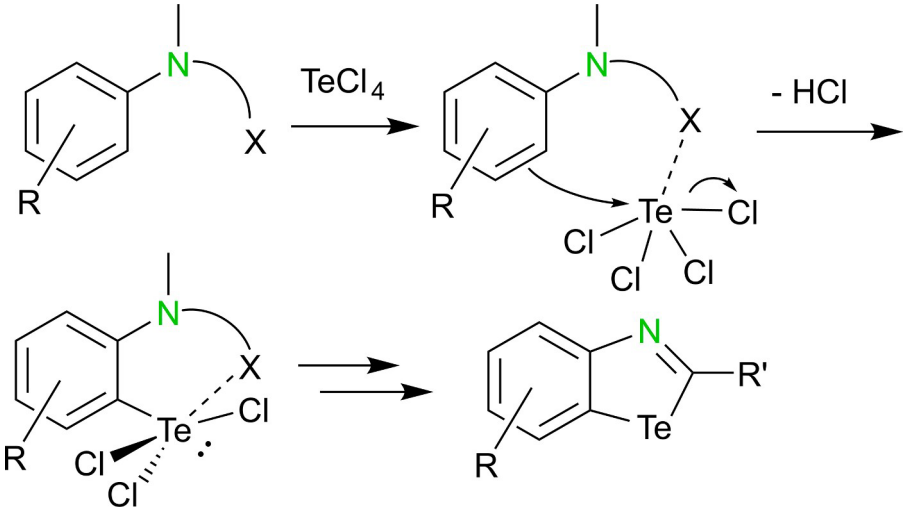
A 100 mL round bottom flask equipped with magnetic stirring, reflux condenser and gas vent line was charged with tellurium powder (2.0 g, 15.7 mmol, 200 mesh), chloroform (5 mL) and sulfuryl chloride (3 mL, 37 mmol). The mixture was brought to gentle reflux overnight, volatiles were removed by rotary evaporation and the remaining tellurium tetrachloride used without further purification. Yield: quantitative.

2.3. 1-[5-Methyl-2-(trichloro-λ4-tellanyl)phenyl] 3,3-dimethylurea 1a (a representative procedure for preparing ureas 1a-5a)

A 100 mL round bottom flask containing tellurium tetrachloride as prepared previously from 2.0 g tellurium was charged with 3,3-dimethyl-1-(3-methylphenyl)urea (2.93 g, 15.7 mmol) and toluene (8 mL). The flask was fitted with mechanical stirring and a reflux condenser fitted with a gas vent line. The flask was immersed in a 140 °C oil bath and the mixture heated to reflux with vigorous mechanical stirring for 5 hrs. The formation of a thick grey crystalline precipitate was observed. The reaction mixture was allowed to cool and the precipitated product collected by filtration. It was dissolved in 150 mL of warm acetone, traces of insoluble material removed by filtration and the filtrate taken to dryness. The resulting grey crystalline material was sufficiently pure for conversion to **1b**. Yield: 5.4 g (84 %). An analytical sample was prepared by dissolution of the crude product in hot nitromethane, hot centrifugation to remove traces of solids and subsequent crystallization. White crystals, dec. >200 °C. ^{1}H NMR (CD_3COCD_3): δ 2.35(s, 1H), 3.25 (s, 6H), 7.18 (s, 1H), 7.22 (d, 1H), 8.38 (d, 1H), 9.47 (s, 1H). ^{13}C NMR (CD_3COCD_3): δ 21.07, 37.47, 122.01, 127.64, 133.65, 136.31, 137.33, 143.47, 157.70. ^{125}Te NMR (CD_3COCD_3): δ 1229.23 ppm. Selected IR bands (cm $^{-1}$): 3296, 1621, 1569, 1458, 1212. HRMS (*m/z*,%): $[M\text{-}H]^-$ 406.8974 (18.6), 406.9053 (37.1), 406.9131 (18.4), 408.8955 (17.8), 408.9034 (76.6), 408.9113 (49.5), 410.8985 (51.2), 410.9064 (100), 410.9143 (47.4). Anal. Calcd. for $C_{10}H_{13}Cl_3N_2OTe$ (411.18 g mol $^{-1}$): C, 29.21; H, 3.19; N, 6.81. Found: C, 29.17; H, 3.11; N, 6.77.

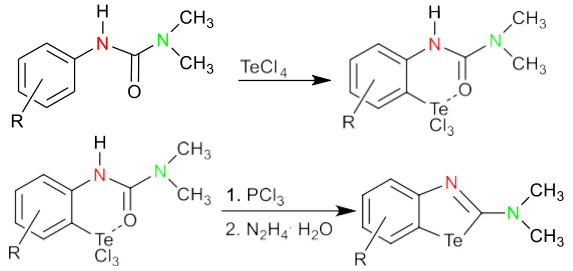
2.4. 1-[4,5-Dimethyl-2-(trichloro-λ^4-tellanyl)phenyl]-3,3-dimethylurea 2a

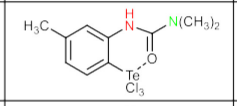
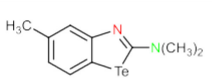
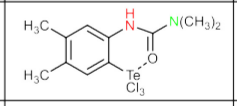
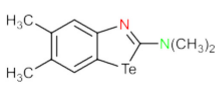
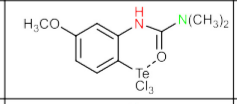
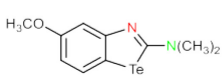
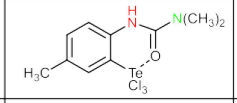
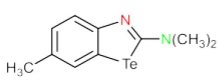
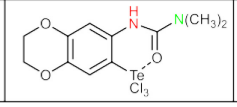
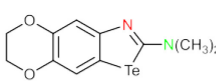
Prepared from 1-(3,4-dimethylphenyl)-3,3-dimethylurea (3.02 g, 15.7 mmol). Off-white crystals, dec. >230 °C. Yield: 5.2 g (78 %). ^{1}H NMR (CD_3COCD_3): δ 2.27 (s, 3H), 2.30 (s, 3H), 3.26 (s, 6H), 7.13 (s, 1H), 8.22 (1H), 9.43 (1H). ^{13}C NMR (CD_3COCD_3): δ 19.34, 19.62, 37.44, 122.37, 122.44, 133.88, 135.28, 135.45, 136.14, 142.26. ^{125}Te NMR (CD_3COCD_3): δ 1229.57 ppm. Selected IR bands (cm $^{-1}$): 3368, 1621, 1560, 1219. HRMS (*m/z*,%): $[M\text{-}H]^-$ 420.9228 (28.0), 422.9148 (59.0), 422.9228 (57.4), 424.9115 (29.6), 424.9195 (100), 424.9276 (43.9),



Scheme 1. Concept of 1,3-benzotellurazole synthesis via coordination assisted regiospecific ortho tellurination, *X* = coordinating moiety.

Table 1
Products prepared in this study.



#	Ureas **a**	Tellurazoles **b**
1a, b		
2a, b		
3a, b		
4a, b		
5a, b		

426.9129 (39.8), 426.9210 (53.1), 426.9290 (17.4). Anal. Calcd. for $C_{11}H_{15}Cl_3N_2OTe$ (425.21 g mol ^{1}): C, 31.07; H, 3.56; N, 6.59. Found: C, 31.06; H, 3.51; N, 6.98.

2.5. 1-[5-Methoxy-2-(trichloro-λ^4-tellanyl)phenyl]-3,3-dimethylurea 3a

Prepared from 1-(3,4-dimethylphenyl)-3,3-dimethylurea (3.05 g, 15.7 mmol). Off-white crystals, dec. >220 °C. Yield: 4.5 g (67 %). ^{1}H NMR (CD_3COCD_3): δ 3.26 (s, 6H), 3.85 (s, 1H), 6.91 (d, 1H), 6.99 (d of d's, 1H), 8.41 (d, 1H), 9.52 (s, 1H). ^{13}C NMR (CD_3COCD_3): δ 37.47, 56.14, 106.55, 112.91, 130.53, 139.16, 157.79, 163.04. ^{125}Te NMR (CD_3COCD_3): δ 1238.33 ppm. Selected IR bands (cm ^{1}): 3353, 1625, 1450, 1293, 1212. HRMS (*m/z*,%): [M-H]$^-$ 422.8987 (33.5), 422.9067 (30.5), 424.8954 (52.3), 424.9034 (77.1), 424.9115 (30.9), 426.8967 (80.4), 426.9048 (100), 426.9129(24.6), 428.8947 (47.3), 428.9028 (63.3), 428.9109 (19.9), 430.8973 (17.3). Anal. Calcd. for $C_{10}H_{13}Cl_3N_2O_2Te$ (427.18 g mol ^{1}): C, 28.12; H, 3.07; N, 6.56. Found: C, 28.13; H, 3.03; N, 6.62.

2.6. 1-[6-Methyl-2-(trichloro-λ^4-tellanyl)phenyl] 3,3-dimethylurea 4a

Prepared from 3,3-dimethyl-1-(4-methylphenyl)urea (2.93 g, 15.7 mmol). Off-white crystals, dec. >200 °C. Yield: 3.2 g (50 %). ^{1}H NMR (CD_3COCD_3): δ 2.39 (s, 3H), 3.27 (s, 6H), 7.26 (d, 1H), 7.32 (d, 1H), 8.31 (s, 1H), 9.58 (s, 1H). ^{13}C NMR (CD_3COCD_3): δ 20.89, 37.46, 121.83, 133.48, 133.59, 135.15, 136.68, 139.20, 157.76. ^{125}Te NMR (CD_3COCD_3): δ 1225.14 ppm. Selected IR bands (cm ^{1}): 3325, 1627, 1512, 1473, 1412. HRMS (*m/z*,%): [M-H]$^-$ 406.9053 (35.9), 408.8955 (17.4), 408.9034 (75.4), 408.9113 (39.3), 410.8985 (49.2), 410.9064 (100), 410.9143 (35.5), 412.8984 (44.0), 412.9064 (57.7), 412.9143 (20.2), 414.9033 (16.6). Anal. Calcd. for $C_{10}H_{13}Cl_3N_2OTe$ (411.18 g mol ^{1}): C, 29.21; H, 3.19; N, 6.81. Found: C, 29.15; H, 3.16; N, 6.63.

2.7. 1-[7-(Trichloro-λ^4-tellanyl)-2,3-dihydro-1,4-benzodioxin-6-yl] 3,3-dimethylurea 5a

Prepared from 1-(2,3-dihydro-1,4-benzodioxin-6-yl)-3,3-dimethylurea (3.49 g, 15.7 mmol). White crystals, dec. > 258 °C. Yield: 5.6 g (79 %). ^{1}H NMR (CD_3COCD_3): δ 3.25 (s, 6H), 4.32-4.37 (m, 4H), 6.84 (s, 1H), 7.99 (s, 1H), 9.43 (s, 1H). ^{13}C NMR (CD_3COCD_3): δ 37.42, 65.21, 65.73, 109.7, 122.26, 131.32, 131.83, 142.64, 147.57, 157.80. ^{125}Te NMR (CD_3COCD_3): δ 1230.24 ppm. Selected IR bands (cm ^{1}): 3307, 2933, 2257, 1625, 1578, 1452, 1411. HRMS (*m/z*,%): [M-H]$^-$ 449.8938 (15.5), 450.8896 (32.3), 450.8979 (40.9), 451.8949 (18.2), 452.8847 (26.9), 452.893 (82.7), 452.9013 (58.1), 454.8841 (25.3), 454.8925 (100), 454.9008 (93.7), 456.888 (43.5), 456.8963 (74.9). 456.9047 (23.7), 458.8962 (16.2). Anal. Calcd. For $C_{11}H_{13}Cl_2N_2O_3Te$ (455.19 g mol ^{1}). C, 29.03; H, 2.88; N, 6.15. Found: C, 28.97; H, 2.75; N, 6.08.

2.8. N,N,5-Trimethyl-1,3-benzotellurazol-2-amine 1b (a representative procedure for preparing tellurazoles 1b-5b)

A 10 mL round bottom flask equipped with reflux condenser and magnetic stirring was charged with 1-[5-methyl-2-(trichloro-λ^4-tellanyl) phenyl] 3,3-dimethylurea (616.8 mg, 1.5 mmol), phosphorus trichloride (412 mg, 3 mmol) and hexamethylphosphoric triamide (HMPA, 1 g). The mixture was heated with stirring to 180° in a Wood's metal bath for 40 min. The flask was removed, allowed to cool to room temperature and carefully neutralized with conc. aqu. sodium bicarbonate solution (foaming!). Hydrazine hydrate (225 mg, 4.5 mmol) and dichloromethane (DCM, 5 mL) were added and the mixture transferred to a centrifuge tube. The organic phase was collected and the aqueous

phase extracted with another 3 mL of DCM. The solvent was removed from the combined extracts and the remaining crude product washed with water to remove remaining traces of HMPA. After drying it was extracted with 2×5 mL of hot heptane. The product was further purified by flash chromatography (DCM:silica gel) to remove highly polar impurities. This was followed by recrystallization from 95 % ethanol. Pale yellow crystals, yield: 360 mg (83 %), mp 122-123 °C. ^{1}H NMR ($CDCl_3$): 2.39 (s, 3H), 3.14 (s, 6H), 6.73 (d of d's, 1H), 7.47 (d, 1H), 7.48 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 21.23, 41.96, 121.87, 122.18, 124.30, 130.32, 137.02, 160.67, 164.59. ^{125}Te NMR ($CDCl_3$): δ 673.83 ppm. Selected IR bands (cm $^{-1}$): 2906, 2857, 1536, 1401, 1343, 1277. HRMS (*m/z*,%): [*M* + *H*]$^{+}$ 285.0162 (16.6), 286.0067 (15.8), 286.0133 (35.1), 287.0055 (24.0), 287.0121 (66.1), 287.0188 (37.8), 289.0084 (40.9), 289.0151 (93.3), 289.0217 (28.0), 290.0192 (18.1), 291.0116 (53.1), 291.0183 (100), 292.0192 (21.8). Anal. Calcd. for $C_{10}H_{12}N_2Te$ (287.82 g mol $^{-1}$): C, 41.73; H, 4.20; N, 9.73. Found: C, 41.59; H, 4.21; N, 9.66.

2.9. N,N,5,6-Tetramethyl-1,3-benzotellurazol-2-amine 2b

Pale yellow crystals, yield 330 mg (73 %), mp 134-135 °C. ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H), 2.29 (s, 3H), 3.14 (s, 6H), 7.35 (s, 1H), 7.45 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 19.31, 19.81, 41.96, 122.16, 124.62, 129.69, 131.09, 135.73, 158.89, 263.02. ^{125}Te NMR ($CDCl_3$): δ 670.13 ppm. (Selected IR bands (cm $^{-1}$): 2858, 1602, 1556, 1445, 1415. HRMS (*m/z*, %): [*M* + *H*]$^{+}$ 299.0261 (23.3), 299.0328 (14.1), 300.0271 (33.2), 300.0338 (25.9), 301.0229 (32.9), 301.0297 (85.1), 301.0229 (32.9), 301.0297 (85.1), 303.0265 (63.6), 303.0333 (100), 304.0341 (22.7), 305.023 (16.5), 305.0298 (88.3), 305.0367 (77.7), 306.034 (26.5). Anal. Calcd. for $C_{11}H_{14}N_2Te$ (301.84 g mol $^{-1}$): C, 43.77; H, 4.68; N, 9.28. Found: C, 43.84; H, 4.73; N, 9.31.

2.10. 5-Methoxy-N,N-dimethyl-1,3-benzotellurazol-2-amine 3b

The reaction temperature was set to 160 °C in this case. White crystals, yield 180 mg (40 %), mp 123-124 °C. ^{1}H NMR ($CDCl_3$): δ 1.15 (s, 6H), 3.83 (s, 3H), 6.56 (d of d's, 1H), 7.23 (d, 1H), 7161.63.43 (, 1H). ^{13}C NMR ($CDCl_3$): δ 41.96, 55.37, 105.69, 109.42, 117.59, 130.74, 160.04, 161.63, 165.53. ^{125}Te NMR ($CDCl_3$): δ 675.37 ppm. Selected IR bands (cm $^{-1}$): 2934, 1532, 1397, 1262, 1121. HRMS (*m/z*,%): [*M* + *H*]$^{+}$ 301.0094 (19.0), 302.0069 (29.2), 302.0137 (17.4), 303.0061 (57.1), 303.0129 (41.3), 305.0025 (28.0), 305.0093 (90.4), 305.0162 (28.3), 306.0135 (16.5), 307.0055 (36.9), 307.0124 (100), 308.0129 (19.6). Anal. Calcd. for $C_{10}H_{12}N_2OTe$ (303.81 g mol $^{-1}$): C, 43.77; H, 4.68; N, 9.28. Found: C, 43.84; H, 4.73; N, 9.31.

2.11. N,N,6-Trimethyl-1,3-benzotellurazol-2-amine 4b

Yield 387 mg (90 %). This compound was identical to a sample previously prepared by an alternate method [26].

2.12. N,N-Dimethyl-10,13-dioxa-4-tellura-6-azatricyclo[7.4.0.0^{3,7}] trideca-1(9),2,5,7-tetraen-5-amine 5b

The product was extracted with hot toluene instead of heptane in this case. White crystals, yield 116 mg (22 %), mp 227-229 °C. ^{1}H NMR ($CDCl_3$): δ 3.12 (s, 6H), 4.23 (d, 2H), 4,25 (d, 2H), 7.03 (s, 1H), 7.17 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 41.88, 64.28, 64.42, 109.22, 117.98, 118.61, 138.65, 143.60, 155.31, 163.28. ^{125}Te NMR ($CDCl_3$): δ 693.57 ppm. Selected IR bands (cm $^{-1}$): 2867, 1535, 1418, 1395 1247. HRMS (*m/z*, %): [*M* + *H*]$^{+}$ 329.0033 (17.5), 330.0036 (31.8), 330.9982 (39.1), 331.0053 (53.7), 332.9991 (45.9), 333.0063 (79.0), 334.0054 (17.6), 332.9991 (45.9), 333.0063 (79.0), 334.9989 (20.1), 335.006 (100), 336.0082 (17.9). Anal. Calcd. for $C_{11}H_{12}N_2O_2Te$ (331.83 g mol $^{-1}$): C, 39.82; H, 3.65; N, 8.44. Found: C, 39.76; H, 3.63; N, 8.41.

3. Results and discussion

The preparation of tellurium tetrachloride is not essential since this compound is commercially available, but on-demand preparation using the procedure described above was found to more economical and practical since it minimizes the handling and storage of this highly hygroscopic compound. Tellurination of ureas required vigorous mechanical stirring and an oil bath to break up residual reactant lumps and avoid localized overheating. Intramolecular Te-O coordination of tellurinated ureas **1a-5a** imparts properties that significantly deviate from those of non-coordinated aryltellurium trichlorides, which typically are yellow, hydrolyze in water and react with acetone to form α-substitution products [27]. While the preparation of ureas **1a–5a** with sufficient purity for subsequent cyclization posed no problems, the preparation of analytically pure samples was challenging due to a tendency of these compounds to retain trace impurities during recrystallization. In pure form they are white, but usually present as grey to light brown crystalline solids with some variability in their elemental analyses.

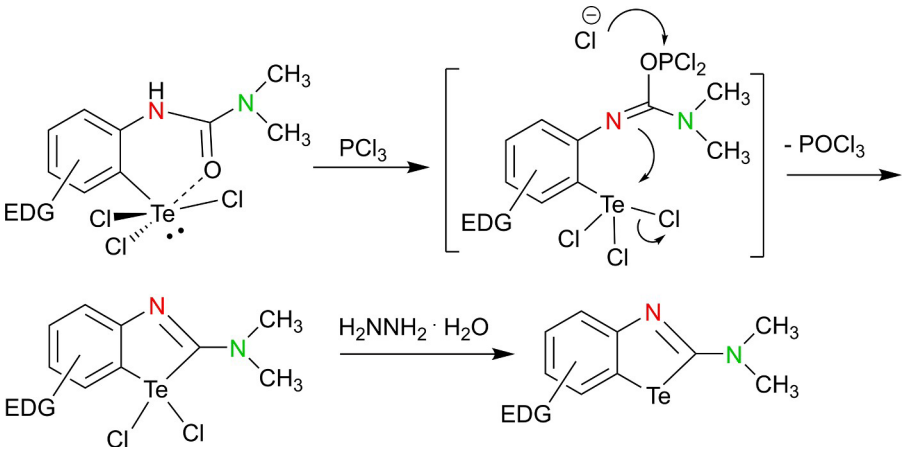
Te-O coordination exerts a strong ortho directing effect, best exemplified by **4a**. In this case coordination overcomes the ortho/para directing effect of the pre-existing methyl group, resulting in regiospecific tellurination ortho to the urea moiety. Attempts to apply the tellurination procedure reported here to 1-dimethyl-3-(*m*-tolyl) thiourea were unsuccessful, likely due to weaker Te-S vs. Te-O coordination. Likewise, 3-[5-methyl-2-(trichloro-λ^{4}-tellanyl)phenyl]-1-phenylurea only generated traces of the corresponding tellurazole, indicating that only trisubstituted ureas cyclize under the conditions applied here. The replacement of electron donating substituents by an electron withdrawing nitro group blocked tellurination. Likewise, attempts to replace HMPA by sulfolane failed. ^{125}Te NMR shifts of 1225-1238 ppm for **1a-5a** are similar to that reported for R)-[2-(4-ethyl-2-oxazolinyl) phenyl]tellurium(IV) trichloride [28], but less shielded than those reported for non-coordinated aryltellurium trichlorides [29,30].

The procedure reported here for the cyclization of o-trichlorotellurophenyl urea derivatives to 1,3-benzotellurazole derivatives appears to have no direct counterpart in sulfur or selenium chemistry. However, phenylureas bearing a methylmercapto moiety in ortho position were reported to cyclize to 1,3-benzothiazoles under the influence of phosgene [31]. A proposed mechanism for the cyclization employed here is shown in Scheme 2. The proposed intermediacy of 1,1-dichloro derivatives is based on the fact that only traces of product were isolated without the addition of hydrazine hydrate during workup. The method reported here appears to be related to the previously reported synthesis of 2-N,N-dialkylamino-1,3-benzotellurazole derivatives from bis(2-aminophenyl) ditelluride and dialkyl formamides [26], with the notable difference that evidence was found for a radical mechanism in that case. In contrast, the cyclizations described here appear to follow a polar pathway. Additions of azobisisobutyronitrile, a common radical initiator, had no effect on product yields. The conditions under which the products in this study were prepared confirm their high stability to heat and air, as previously observed for similar 2-N,N-dialkylamino-1,3-benzotellurazole derivatives [26].

3.1. Crystallographic characterizations of 3a and 1b

An ellipsoid plot of compound **3a** is shown in Fig. 1.

Compounds **3a** and **1b** constitute one representative example each of intermediate 1-[2-(trichlorotellanyl)phenyl] 3,3-dimethylureas and the targeted 1,3-benzotellurazole derivatives prepared in this study. Compound **3a** crystallized in space group $P2_{1/n}$ with one molecule in the asymmetric unit and exhibits strong intramolecular Te-O coordination. At 2.2228(12) Å, the Te1-O1 distance is significantly shorter than the sum of the elements' van der Waals radii but longer than 1.819-2.115 Å reported for covalent bonds found in TeO_2 polymorphs [32]. The presence of a lone pair creates in a square pyramidal geometry around the Te atom. The Cl1, Cl2, Cl3, Te1 and O1 atoms are nearly coplanar (relative



Scheme 2. Proposed mechanism for the cyclization of 1-[2-(trichloro-λ^4-tellanyl)phenyl] 3,3-dimethylurea derivatives to 2-N,N-dimethylaminophenyl-1,3-benzotellurazoles.

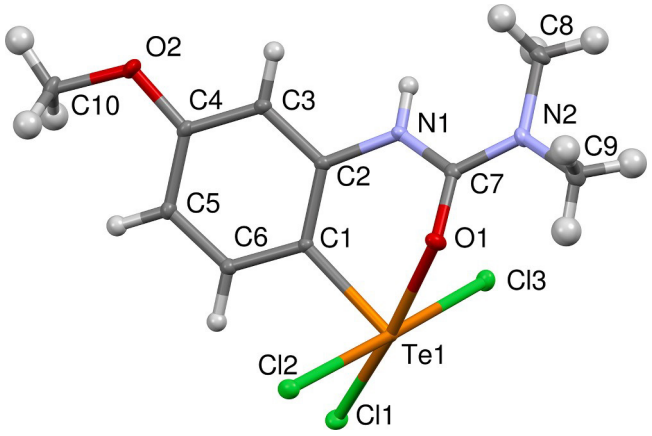


Fig. 1. Ellipsoid plot of 1-[5-Methyl-2-(trichloro-λ^4-tellanyl)phenyl] 3,3-dimethylurea 3a. Selected bond lengths: Te1-C1, 2.1108(13) A; Te1-O1, 2.2228 (12) Å; Te1-Cl1, 2.4633(10) Å; Te1-Cl2, 2.6085(8) Å; Te1-Cl3, 2.4622(7) Å; N1-C7, 1.3554(16) Å. Selected angles Cl2-Te1-Cl3, 178.368(10)°; O1-Te1-Cl1 169.99(2)°.

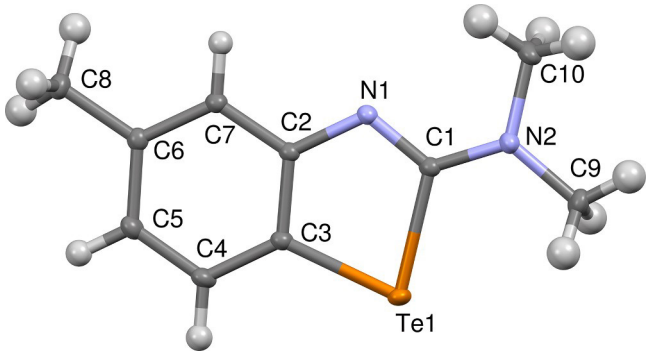


Fig. 2. Ellipsoid plot of N,N,5-trimethyl-1,3-benzotellurazol-2-amine 1b. Selected bond lengths: Te1-C1, 2.125(1) Å; C1-N1,1.299(2) Å; N2-C1, 1.346 (2) Å. Torsional: C10-N2-C1-Te1 angle, 173.83(**10**)°.

mean standard deviation from planarity=0.07 Å). Intramolecular coordination of tellurium by functional groups including oxazolinyl, amino, imino, pyridyl and carbonyl moieties is a recurring theme [28] while intermolecular Te···O coordination of chlorinated isotellurazole N-oxides resulted in supramolecular aggregates [33]. The observed Te-O coordination in **3a** likely accounts for the regiospecific ortho tellurination. The C7-N2 bond length of 1.334(2) Å indicates partial double bond character, as confirmed by the presence of broadened -N$(CH_3)_2$ signals in ^{1}H NMR spectra for this class of compounds due to hindered rotation.

Compound **1b** crystallized in space group $P2_12_12$ with one molecule in the asymmetric unit. All non-H atoms are nearly coplanar and lack intermolecular secondary Te···N bonding interactions that were reported for other 1,3-benzotellurazoles [34] (Fig. 2).

4. Conclusions

An efficient two-step procedure has been developed to prepare previously inaccessible 1,3-benzotellurazole derivatives carrying electron donating moieties in the benzene ring. The method presented here is based on electrophilic ortho tellurination, mediated by Te-O coordination of electron rich phenyl ureas with tellurium tetrachloride and subsequent cyclization with phosphorus trichloride. It employs readily accessible starting materials. A representative product, N,N,5-trimethyl-1,3-benzotellurazol-2-amine, was characterized by X-ray crystallography. It lacks Te···N intermolecular secondary interactions that were reported for other 1,3-benzotellurazoles.

Data availability

The full crystallographic data for **3a** and **1b** have been deposited in CIF format at the Cambridge Crystallographic Data Centre as CCDC2362089 and CCDC2362090

CRediT authorship contribution statement

Killian M. Gaborit: Writing - review & editing, Investigation. **Alanna K. Turner:** Investigation. **Samantha R. Ponzo:** Investigation. **Frank R. Fronczek:** Writing - review & editing, Investigation, Formal analysis, Data curation. **Thomas Junk:** Writing - original draft, Supervision, Project administration.

Declaration of competing interest

The authors declare no competing interests.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2024.123342.

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