Studies on Tellurium-Containing Heterocycles. Part 22.[1] Tellurazepine Ring System: Preparation of 1,5-Benzotellurazepin-4-ones and Their Conversion into Fully Unsaturated 1,5-Benzotellurazepines

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The treatment of *o*-iodopropiolanilides (12), which were easily prepared from *o*-iodophenylisocyanate (11) and ethynylmagnesium bromide, with sodium hydrogen telluride resulted in the intramolecular ring closure of the presumed phenyltellurol intermediates (13) to a triple bond to give the 1,5-benzotellurazepin-4-ones (14) as the sole characterized products. The obtained amides (14) were easily converted into fully unsaturated lactim 4-methoxy-1,5-benzotellurazepines (18) by treatment with trimethyloxonium tetrafluoroborate. Decomposition by thermolysis of the 4-methoxyazepinenes (18) afforded the 4-methoxyquinolines (19) with extrusion of a tellurium atom.

Key words 1,5-benzotellurazepin-4-one; 1,5-benzotellurazepine; intramolecular cyclization; phenyltellurol; triple bond

The chemistry of the thiazepine ring systems, seven-membered heterocycles containing atoms of both sulfur and nitrogen has been reviewed.[2—6] Monocyclic 1,4-thiazepine compounds (**1**, **2**) have been prepared by the Schmidt ring-expansion of 4*H*-thiopyran-1,1-dioxides[7] and by the Beckmann rearrangement of thiapyran-4-one oxime.[8] The syntheses of its benzo derivatives, the 1,5-benzothiazepines (**3**), were described by Hofmann and Fischer[9,10] and by Kaupp *et al.*[11] The procedure for the preparation of these compounds is the *cis*-addition of *o*-mercaptoaniline to propiolic acid, followed by the cyclization of the adducts. 1,4-Benzothiazepines (**4**)[12] have also been produced by the condensation of 2-mercaptobenzamide and bromoacetaldehyde diethylacetal. Furthermore, the photocycloaddition of 2-phenylbenzothiazole with acetylenes gave the 1,5-benzothiazepines (**5**)[13] in one step. In addition, a number of tellurium-nitrogen-containing heterocycles[14] have been prepared. However, only two papers[15,16] have been published to date on the synthesis of seven-membered tellurazepine rings. 1,4-Dibenzo[*b*,*f*]tellurazepine (**7**)[15] was prepared by the thermolysis of 9-azidoxanthene (**6**) in 1987. The one-pot synthesis of the 2-aryl-1,5-benzotellurazepines (**9**)[16] has been reported based on the condensation of sodium 2-aminophenyltellurolate (**8**) with arylpropargyl aldehydes.

In recent years, we have been investigating the syntheses of the 3-benzotellurepines[17] and 1-benzotellurepines,[18,19] novel fully unsaturated seven-membered heterocycles containing a tellurium atom. More recently, a convenient synthetic route for the preparation of tellurochromones,[20] six-membered tellurium-containing carbonyl compounds, was also reported. Our synthetic strategy[21,22] for the preparation of these compounds is based on the intramolecular cyclization of the tellurol moieties to a triple bond. In this respect, we report herein the synthesis of the title compounds[23] as an extension of increasing interest in our methodology for preparing the tellurium-containing heterocycles.

The first sub-goal is the preparation of the tellurazepinones (**14**). The preparation of **14** from *o*-iodobenzoic acid (**10**) is shown in Chart 3. *o*-Iodophenylisocyanate (**11**) was easily prepared from **10** *via* one-step according to the diphenylphospholic azide (DPPA) procedure reported by Shioiri and Yamada[24] in almost quantitative yield. The successful reaction of the isocyanate (**11**) with Grignard reagents was a result of the sp^2–sp carbon–carbon bond formation to afford the *o*-iodopropiolanilides (**12**), the key starting compounds for the synthesis of the tellurazepinones (**14**). Compound **11** reacted with one equivalent of an alkynylmagnesium bromide in tetrahydrofuran (THF) at 0 °C to give the corresponding anilides (**12**) as the sole product in moderate to good yields. The telluration of the *o*-iodopropiolanilides (**12**) *via* the lithium compound, which was the method for the preparation of the 1-benzotellurepines, was unsuccessful. Therefore, we examined our original telluration method for the construction

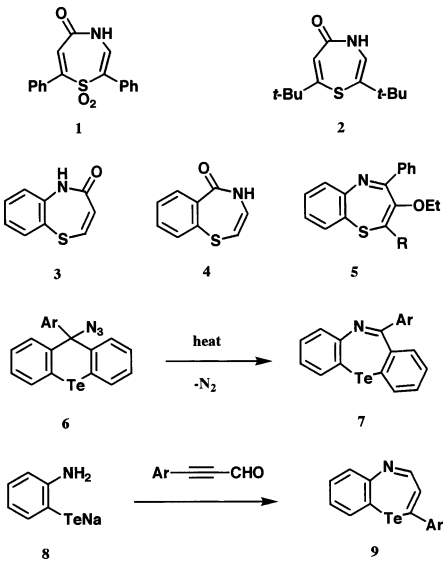

Chart 1

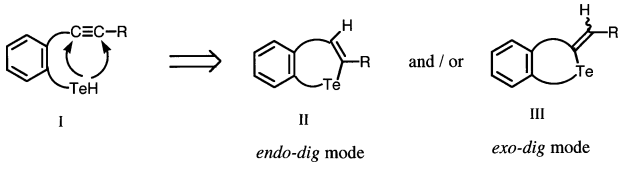

Chart 2

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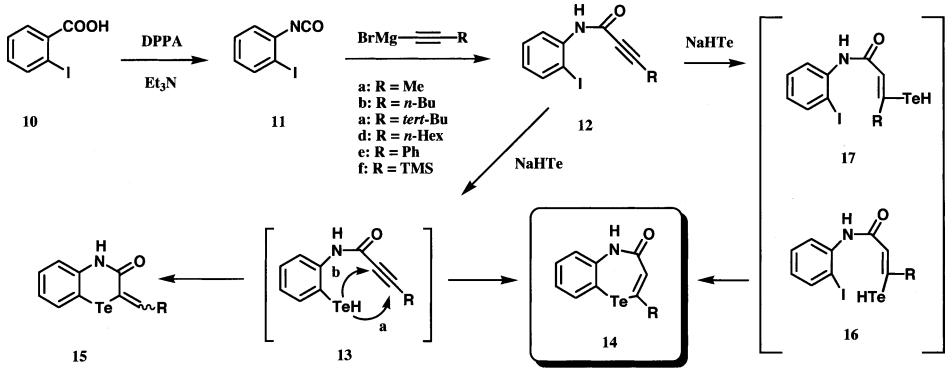

Chart 3

Table 1. 1,5-Benzotellurazepin-4-ones (**14**)

Conpound No.	R	Yield (%)	Appearance (mp °C)
14a	Me	19	Pale yellow prisms (118—120)
14b	*n*-Bu	26	Pale yellow prisms (148—150)
14c	*tert*-Bu	29	Pale yellow prisms (150—151)
14	*n*-Hex	25	Yellow prisms (172—174)
14e	Ph	26	Pale yellow prisms (184—186)
14f	TMS	Trace	Pale yellow prisms (96—98)

of the 1,5-benzotellurazepine skeleton, and applied the one-pot method for the preparation of the tellurochromones[20] from the *o*-bromophenylethynyl ketones described in our previous paper. The treatment of the propiolanilides (**12**) with sodium hydrogen telluride (NaHTe),[25] generated *in situ* from tellurium powder and sodium borohydride in dimethylformamide (DMF) at *ca.* 100 °C, resulted in the direct ring closure to afford the desired 1,5-benzotellurazepin-4-ones (**14**) as the sole characterized product. The results of this ring closure for the preparation of **14** are shown in Table 1. 2-Alkyl- (**14a**—**d**), 2-phenyl- (**14e**) and 2-trimethylsilyl (TMS)-tellurazepinones (**14f**) were obtained as stable yellow crystalline products with an unknown complex mixture, while the yields of the expected tellurazepines (**14**) were not good. Especially, the TMS derivative (**14f**) was isolated in only a trace amount, probably because of the thermal instability of **14** itself and its desylilated parent product, which might be produced under such conditions. The obtained tellurazepinones (**14**) are novel compounds, and were characterized on the basis of the spectral data (Table 2). Neither the presumable phenyltellurole intermediates (**13**) nor their oxidized dimeric-type products, the ditellurides, were obtained. The tellurazepinones (**14**) were produced by the Michael-type 7-*endo-dig* ring closure of the tellurols (**13**) at the *sp* carbon atom of the triple bond; the 6-*exo-dig* reaction products (**15**) were not formed.

An alternative mechanism for the formation of **14** would involve the addition of NaHTe to an alkynyl moiety to first produce the *Z*-vinyltellurols (**16**). However, this possibility was eliminated by the facts that the regio isomers, *E*-vinyltellurols (**17**), which might not cyclize to form the tellurazepines (**14**), and their corresponding oxidized ditellurides were not produced. If the first step of the reaction is the Michael-type addition of NaHTe to the ynone function of **12**, the adducts (**16**, **17**) should be generated in the same ratio. In addition,[23] the reaction of the propiolanilide having no halogen group at the *ortho* position with NaHTe under the same reaction conditions used for the preparation of **14** did not afford any adducts or the corresponding ditellurides. It is reported[25] that an electron-withdrawing group at the resonance position on an aromatic ring could significantly enhance the reactivity of the nucleophilic substitution of the iodo anion with the hydrotelluro group, however, an electron-donating group decreased; *e.g.*, *p*-aminoiodobenzene did not react with NaHTe to give the *p*-aminophenyl tellurol or the corresponding ditelluride. The starting material was recovered. For the reaction of the propiolanilides (**12**) with NaHTe, the replacement of the iodo anion by the hydrotelluro group would proceed because of the decreased electron-donating inductive effect due to the change in the amino group to the amide such as a propiolalnilide.

In order to introduce the conjugated double bond, the lactams (**14b**—**e**) were treated with trimethyloxonium tetrafluoroborate ($Me_3O^+ BF_4^-$) in dichloromethane at 0 °C to give the 4-methoxy-1,5-benzotellurazepines (**18b**—**e**) in *ca.* 40—45% yields. 2-Methyltellurazepine (**18a**) was essentially formed and detected on TLC, however, it could not be isolated. **18a** was decomposed during the normal isolating operation because of its thermal instability. Compounds (**18b**—**e**) are somewhat unstable, and gradually decomposed during storage at room temperature even under argon. It is well known that simple monocyclic thiepines, selenepines and benzotellurepines[13] are thermally unstable due to the easy extrusion of the hetero elements, but the stability of the heteropine ring can be enhanced by the introduction of a bulky group into the α-position. We next examined a few reactions of the new 1,5-benzotellurazapinene rings using **14** and **18** for comparison with the 1-benzotellerepines,[13] whose reactivity was described in our previous report. However, the halogenation with SO_2Cl_2, Br_2 or I_2 and the oxidation of the tellurazepines (**14**, **18**) gave a complex mixture without any characterized products. The reactions of **14** and **18** with lithium reagents or Grignard reagents also afforded no characterized products. The pyrolysis of **18** at 160 °C in mesitylene for *ca.* 1 h resulted in the exclusion of the Te element to yield the 2-methoxyquinolines (**19b**—**d**) in good yields. Upon heating under these conditions, the 2-phenyltellurazepinone (**18e**) af-

Table 2. Spectral Data for the 1,5-Benzotellurazepin-4-ones (**14**)

Compound No. R	Formula MS (*m/z*: M^+)	IR cm^{-1}	^{1}H-NMR (500 MHz, *J*=Hz) 3-H	NH	Ph–H	R–H
14a R=Me	$C_{10}H_9NOTe$ (289)	3176 (NH) 1646 (C=O)	6.54 (q, *J*=1.8)	9.39 (br s)	7.07 (1H, dd, *J*=7.3, 7.8) 7.26 (1H, *J*=7.8) 7.35 (1H, dd, *J*=7.3, 7.8) 7.80 (1H, d, *J*=7.8)	2.48 (3H, d, *J*=1.8) Me
14b R=*n*-Bu	$C_{13}H_{15}NOTe$ (331)	3150 (NH) 1654 (C=O)	6.55 (s)	9.39 (br s)	7.06 (1H, dd, *J*=7.3, 7.8) 7.26 (1H, d, *J*=7.8) 7.34 (1H, dd, *J*=7.3, 7.8) 7.80 (1H, d, *J*=7.8)	0.89 (3H, t, *J*=7.3) 1.26—1.33 (2H, m) 1.47—1.51 (2H, m) 2.60 (2H, t, *J*=7.3) *n*-Bu
14c R=*tert*-Bu	$C_{13}H_{15}NOTe$ (331)	3176 (NH) 1652 (C=O)	6.58 (s)	8.09 (br s)	7.05 (1H, dd, *J*=7.3, 7.8) 7.16 (1H, d, *J*=7.8) 7.36 (1H, dd, *J*=7.3, 7.8) 7.87 (1H, d, *J*=7.8)	1.18 (9H, s) *tert*-Bu
14d R=*n*-Hex	$C_{15}H_{19}NOTe$ (359)	3162 (NH) 1627 (C=O)	6.54 (s)	9.03 (br s)	7.06 (1H, dd, *J*=7.3, 7.8) 7.24 (1H, d, *J*=7.8) 7.35 (1H, dd, *J*=7.3, 7.8) 7.80 (1H, d, *J*=7.8)	0.86 (3H, t, *J*=7.3) 1.25—1.29 (6H, m) 1.48—1.52 (2H, m) 2.59 (2H, *J*=7.3) *n*-Hex
14e R=Ph	$C_{15}H_{11}NOTe$ (351)	3460 (NH) 1646 (C=O)	7.52 (s)	8.56 (br s)	6.93 (1H, dd, *J*=7.3, 7.5), 6.97 (1H, d, *J*=7.5), 7.18 (1H, dd, *J*=7.3, 7.3), 7.28—7.32 (2H, m), 7.37 (1H, d, *J*=7.5), 7.39—7.7.43 (1H, m), 7.45—7.49 (2H, m) Ph	
14f R=TMS	$C_{12}H_{15}NOSiTe$ (347)	3192 (NH) 1650 (C=O)	8.15 (s)	8.2 (br)	6.81 (1H, d, *J*=8.0) 6.94 (1H, dd, *J*=7.7, 7.7) 7.18 (1H, dd, *J*=8.0, 7.7) 7.44 (1H, d, *J*=7.7)	0.24 (9H, s) TMS

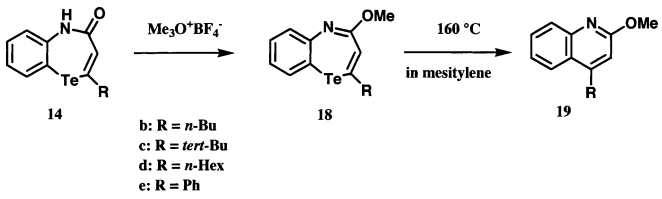

Chart 4

forded no isolable products, and gradually decomposed. The tellurazepinones (**14**) were quite stable without decomposition in refluxing mesitylene.

In conclusion, the construction of the 1,5-benzotellurazepine ring system was achieved using the intramolecular cyclization of the tellurol to a triple bond. The obtained novel tellurazepinones were transformed into the fully unsaturated 4-methoxy-1,5-benzotellurazepines, which were decomposed to afford the quinoline derivatives with their ready tellurium extrusion. Neither the selenium and sulfur seven-membered analogues could be obtained using similar methods.

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 HR-MS were recorded on a JEOL JMS-DX300 instrument. ^{1}H-NMR spectra were determined with a JEOL PMX-60SI (60 MHz), a JEOL EX-90A (90 MHz) or a JEOL ECP-500 (500 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as internal standard; *J* values are given in Hz. ^{13}C-NMR spectra were recorded on a JEOL ECP-500 (125 MHz) spectrometer. Microanalyses were performed in the Microanalytical Laboratory of this Faculty.

Preparation of *o*-Iodophenylisocyanate (11) DPPA (82.6 g, 0.3 mol) was added to a mixture of *o*-iodobenzoic acid (**10**, 74.4 g, 0.3 mol) and triethylamine (30.3 g, 0.3 mol) in benzene (300 ml) at 0 °C under an argon atmosphere. The reaction mixture was stirred under the same conditions for 2 h, and then washed with water (300 ml×3), brine and dried ($MgSO_4$). The benzene solution was heated to refluxing temperature for 1—2 h, and evaporated *in vacuo* to give crude isocyanate (**11**) as a pale yellow oil in almost quantitative yield.

IR (neat) cm^{-1}: 2260 (N=C=O). **11** was immediately used for the next step without purification.

Preparation of *o*-Iodopropiolanilides (12) The above benzene solution (300 ml) of *o*-iodophenylisocyanate (**11**, 0.3 mol) was added to a THF (200 ml) solution of an alkynylmagnesium bromide (0.3 mol), which was freshly prepared from ethylmagnesium bromide (0.3 mol) and the corresponding 1-alkyne (0.3 mol) under an argon atmosphere at 0 °C. The reaction mixture was stirred overnight at room temperature, and quenched by addition of 20% ammonium chloride solution (300 ml). After separation of organic layers, the aqueous layer was extracted with benzene (100 ml×3). The combined organic fraction was washed with 3% H_2SO_4 (150 ml×2), satd. $NaHCO_3$ (100 ml×2) and brine (150 ml×2), and dried ($MgSO_4$). Evaporation of organic solvent *in vacuo* gave the crude product (**12**), which was recrystallized from acetone–*n*-hexane to afford the pure anilides.

12a (R=Me): 48.13 g, 56% yield, pale yellow leaflets, mp 144—146 °C. IR (KBr) cm^{-1}: 3264 (NH), 2240 (C≡C), 1640 (C=O). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 2.27 (3H, s, Me), 7.12, 7.62, 8.07 and 8.43 (1H, ddd, *J*=8, 8, 2 Hz, 1H, ddd, *J*=8, 8, 2 Hz, 1H, dd, *J*=8, 2 Hz, and 1H, br d, *J*=8 Hz, Ph–H), 8.0 (1H, br, NH). MS *m/z*: 285 (M^+, 30), 219 (25), 158 (100), 67 (78). *Anal.* Calcd for $C_{10}H_8NOI$: C, 42.11; H, 2.83; N, 4.91. Found: C, 41.93; H, 2.63; N, 4.90.

12b (R=*n*-Bu): 58.90 g, 60% yield, colorless leaflets, mp 77—80 °C. IR (KBr) cm^{-1}: 3272 (NH), 2236 (C≡C), 1642 (C=O). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.85, 1.1—1.7 and 2.28 (3H, t, *J*=6 Hz, 4H, m, 2H, t, *J*=6 Hz, *n*-Bu), 6.82, 7.32, 7.77 and 8.17 (1H, ddd, *J*=8, 8, 2 Hz, 1H, ddd, *J*=8, 8, 2 Hz, 1H, dd, *J*=8, 2 Hz, and 1H, br d, *J*=8 Hz, Ph–H), 7.7 (1H, br, NH). MS *m/z*: 327 (M^+, 22), 219 (16), 200 (100), 109 (20). *Anal.* Calcd for $C_{13}H_{14}NOI$: C, 47.73; H, 4.31; N, 4.28. Found: C, 47.52; H, 4.05; N, 4.28.

12c (R=*tert*-Bu): 61.8 g, 63% yield, colorless leaflets, mp 65—67 °C. IR (KBr) cm^{-1}: 3262 (NH), 2228 (C≡C), 1658 (C=O). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.30 (9H, s, *tert*-Bu), 6.88, 7.40, 7.83 and 8.20 (1H, ddd, *J*=8, 8, 2 Hz, 1H, ddd, *J*=8, 8, 2 Hz, 1H, dd, *J*=8, 2 Hz, and 1H, br d, *J*=8 Hz, Ph–H), 7.7 (1H, br, NH). MS *m/z*: 327 (M^+, 21), 200 (100), 109 (33), 81 (43). *Anal.* Calcd for $C_{13}H_{14}NOI$: C, 47.73; H, 4.31; N, 4.28. Found: C, 47.49; H, 4.07; N, 4.26.

12d (R=*n*-Hex): 78.54 g, 74% yield, pale yellow leaflets, mp 55—57 °C. IR (KBr) cm^{-1}: 3272 (NH), 2232 (C≡C), 1640 (C=O). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.90, 1.0—2.0 and 2.33 (3H, t, J=5 Hz, 8H, m, and 2H, t, J=6 Hz, *n*-Hex). 6.83, 7.33, 7.77 and 8.20 (1H, ddd, J=8, 8, 2 Hz, 1H, ddd, J=8, 8, 2 Hz, 1H, dd, J=8, 2 Hz, and 1H, br d, J=8 Hz, Ph–H), 7.9—8.5 (1H, br, NH). MS *m/z*: 355 (M^+, 28), 228 (100), 219 (20). *Anal.* Calcd for $C_{15}H_{18}NOI$: C, 50.71; H, 5.11; N, 3.94. Found: C, 50.55; H, 5.12; N, 3.89.

12e (R=Ph): 66.6 g, 64% yield, yellow prisms, mp 103—104 °C. IR (KBr) cm^{-1}: 3148 (NH), 2212 (C≡C), 1630 (C=O). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 6.88, 7.2—7.6, 7.83 and 8.30 (1H, ddd, J=8, 8, 2 Hz, 6H, m, 1H, dd, J=8, 2 Hz, and 1H, br d, J=8 Hz, Ph–H), 8.0 (1H, br, NH). MS *m/z*: 347 (M^+, 18), 220 (99), 129 (100). *Anal.* Calcd for $C_{15}H_{10}NOI$: C, 51.89; H, 2.90; N, 4.03. Found: C, 51.80; H, 2.99; N, 4.00.

12f (R=TMS): 47.3 g, 46% yield, colorless needles, mp 82—84 °C. IR (KBr) cm^{-1}: 3296 (NH), 2212 (C≡C), 1642 (C=O). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.33 (9H, s, TMS), 6.88, 7.37, 7.83 and 8.20 (1H, ddd, J=8, 8, 2 Hz, 1H, ddd, J=8, 8, 2 Hz, 1H, dd, J=8, 2 Hz, and 1H, br d, J=8 Hz, Ph–H), 7.9 (1H, br, NH). MS *m/z*: 343 (M^+, 20), 216 (100), 125 (22), 97 (19). *Anal.* Calcd for $C_{12}H_{14}NOISi$: C, 41.98; H, 4.11; N, 4.08. Found: C, 42.10; H, 4.02; N, 4.10.

Preparation of 1,5-Benzotellurazepin-4-ones (14) Under an argon atmosphere, a solution of *o*-iodopropiolanilides (**12**, 20 mmol) in DMF (20 ml) was slowly added to a solution of sodium hydrogen telluride (24 mmol), which was prepared from tellurium powder (3.06 g, 24 mmol) and sodium borohydride (1.08 g, 24 mmol) in DMF (80 ml), at 100 °C for 2 h. The whole reaction mixture was stirred under these conditions overnight and poured into cold water (500 ml). The aqueous mixture was filtered and extracted with benzene (200 ml×3). The extracts were washed with water (100 ml×3), brine (50 ml×2) and dried ($MgSO_4$), and then concentrated. The resulting residue was chromatographed on silica gel, eluting with CH_2Cl_2–acetone, to give **14**. Products were recrystallized from *n*-hexane–acetone. The results are given in Table1, HR-MS, IR and ^{1}H-NMR spectral data for **14** are listed in Table 2.

14a (R=Me): HR-MS *m/z*: 288.9850 (Calcd for $C_{10}H_9NOTe$: 288.9746). ^{13}C-NMR ($CDCl_3$) δ: 32.77 (q), 113.39 (s), 123.91 (d), 126.42 (d), 130.15 (d), 132.07 (s), 132.41 (d), 138.89 (d), 141.04 (s), 170.77 (s).

14b (R=*n*-Bu): *Anal.* Calcd for $C_{13}H_{15}NOTe$: C, 47.48; H, 4.60; N, 4.26. Found: C, 47.49; H, 4.54; N, 4.25. ^{13}C-NMR ($CDCl_3$) δ: 13.83 (q), 21.88 (t), 31.31 (t), 44.85 (t), 113.11 (s), 123.75 (d), 126.37 (d), 130.10 (d), 131.07 (d), 138.95 (d), 139.41 (s), 141.27 (s), 170.82 (s).

14c (R=*tert*-Bu): *Anal.* Calcd for $C_{13}H_{15}NOTe$: C, 47.48; H, 4.60; N, 4.26. Found: C, 47.68; H, 4.64; N, 4.12. ^{13}C-NMR ($CDCl_3$) δ: 29.45 (q), 40.63 (s), 113.69 (s), 123.06 (d), 128.01 (d), 129.19 (d), 130.10 (d), 139.34 (d), 141.38 (s), 151.74 (s), 170.59 (s).

14d (R=*n*-Hex): *Anal.* Calcd for $C_{15}H_{19}NOTe$: C, 50.48; H, 5.37; N, 3.92. Found: C, 50.43; H, 5.27; N, 3.95. ^{13}C-NMR ($CDCl_3$) δ: 13.99 (q), 22.44 (t), 28.37 (t), 29.13 (t), 31.49 (t), 45.13 (t), 113.22 (s), 123.69 (d), 126.40 (d), 130.07 (d), 131.02 (d), 138.98 (d), 139.59 (s), 141.18 (s), 170.62 (s).

14e (R=Ph): HR-MS *m/z*: 350.9908 (Calcd for $C_{15}H_{11}NOTe$: 350.9903). ^{13}C-NMR ($CDCl_3$) δ: 118.23 (s), 123.00 (d), 124.06 (d), 124.00 (d), 127.98 (d), 128.28 (d), 128.99 (d), 129.00 (d), 132.75 (d), 137.39 (s), 139.07 (s), 144.70 (s), 163.33 (s).

14f (R=TMS): HR-MS *m/z*: 346.9999 (Calcd for $C_{12}H_{15}NOSiTe$: 346.9985).

Treatment of 14 with Me_3O^+ BF_4^-: Formation of 4-Methoxy-1,5-benzotellurazepines (18) To a solution of the lactam (**14**, 0.2 mmol) in CH_2Cl_2 (10 ml) was added Me_3O^+ BF_4^- (88 mg, 0.6 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature overnight, and then quenched with 10% K_2CO_3 solution. The mixture was extracted with CH_2Cl_2 and washed with brine (50 ml×2) and the extracts were dried ($MgSO_4$). The solvent was removed *in vacuo* and the resulting residue was chromatographed on silica gel using *n*-hexane–CH_2Cl_2 (1 : 2) as an eluent to give **18**.

18b (R=*n*-Bu): 28 mg, 41% yield, colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.87, 1.2—1.5 and 2.55 (3H, t, J=6 Hz, 4H, m, 2H, t, J=7 Hz, *n*-Bu), 3.85 (3H, s, OMe), 6.37 (1H, s, 3-H), 6.9—7.3 and 7.68 (3H, m and 1H, d, J=7 Hz, Ph–H). MS *m/z*: 345 (M^+, 40), 343 (35), 215 (80), 214 (100), 345.0375 (Calcd for $C_{14}H_{17}NOTe$: 345.0372).

18c (R=*tert*-Bu): 31 mg, 45% yield, colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.16 (9H, s, *tert*-Bu), 3.89 (3H, s, OMe), 6.40 (1H, s, 3-H), 6.8—7.4 and 7.75 (3H, m, 1H, d, J=7 Hz, Ph–H). MS *m/z*: 345 (M^+, 40), 343 (35), 215 (75), 214 (100), 200 (34), 186 (27), 345.0285 (Calcd for $C_{14}H_{17}NOTe$: 345.0372).

18d (R=*n*-Hex): 29 mg, 40% yield, colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.85, 1.1—1.6 and 2.54 (3H, t, J=7 Hz, 8H, m, 2H, t, J=7 Hz, *n*-Hex), 3.85 (3H, s, OMe), 6.37 (1H, s, 3-H), 6.9—7.3 and 7.68 (3H, m, 1H, d, J=7 Hz, Ph–H). MS *m/z*: 373 (M^+, 30), 371 (28), 243 (55), 242 (100), 214 (25), 173 (50), 373.0711 (Calcd for $C_{16}H_{21}NOTe$: 373.0685).

18d (R=Ph): 28 mg, 39% yield, colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 3.97 (3H, s, OMe), 6.50 (1H, s, 3-H), 7.1—7.8 (9H, m, Ph–H). MS *m/z*: 365 (M^+, 85), 363 (80), 235 (100), 234 (46), 365.065 (Calcd for $C_{16}H_{13}NOTe$: 365.059).

Thermolysis of Tellurazepine (18): Formation of 2-Methoxyquinoline (19) A solution of tellurazepine (**18**, 0.04 mol) in mesitylene (3 ml) was refluxed for 1 h. After cooling, the mixture was chromatographed on silica gel using CH_2Cl_2 as an eluent to give the 2-methoxyquinolines (**19**).

4-*n*-Butyl-2-methoxyquinoline (**19b**): 6.3 mg, 73% yield, colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.97, 1.3—2.0 and 2.99 (3H, t, J=6 Hz, 4H, m, 2H, t, J=8 Hz, *n*-Bu), 4.06 (3H, s, OMe), 6.75 (1H, s, 3-H), 7.4—8.0 (4H, m, Ph–H). MS *m/z*: 215 (M^+, 100), 214 (98), 186 (48), 185 (35), 173 (55), 215.1313 (Calcd for $C_{14}H_{17}NO$: 215.1310).

4-*tert*-Butyl-2-methoxyquinoline (**19c**): 7.5 mg, 87% yield, colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.58 (9H, s, *tert*-Bu), 4.05 (3H, s, OMe), 6.87 (1H, s, 3-H), 7.3—7.6, 7.89 and 8.29 (2H, m, 1H, d, J=8 Hz and 1H, d, J=8 Hz, Ph–H). MS *m/z*: 215 (M^+, 100), 214 (98), 200 (51), 186 (40), 185 (40), 215.1318 (Calcd for $C_{14}H_{17}NO$: 215.1310).

4-*n*-Hexyl-2-methoxyquinoline (**19d**): 6.5 mg, 67% yield, colorless oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.94, 1.1—2.5 (3H, t, J=7 Hz, 10H, m, *n*-Hex), 3.84 (3H, s, OMe), 6.57 (1H, s, 3-H), 6.8—6.9, 7.5—7.6 and 7.9—8.0 (2H, m, 1H, m, 1H, m, Ph–H). MS *m/z*: 243 (M^+, 100), 242 (98), 214 (29), 173 (49), 243.1603 (Calcd for $C_{16}H_{21}NO$: 243.1623).

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