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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Received November 6, 2003; accepted December 20, 2003

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-dioxides⁷⁾ 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 heterocycles¹⁴⁾ 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-azido-xanthene (**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-benzotellurepines¹⁷⁾ 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 compounds²³⁾ 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 diphenylphosphoric azide (DPPA) procedure reported by Shioiri and Ya-

mada²⁴⁾ 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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Table 1. 1,5-Benzotellurazepin-4-ones (**14**)

Compound No.	R	Yield (%)	Appearance (mp °C)
14a	Me	19	Pale yellow prisms (118—120)
14b	<i>n</i> -Bu	26	Pale yellow prisms (148—150)
14c	<i>tert</i> -Bu	29	Pale yellow prisms (150—151)
14d	<i>n</i> -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 tellurochromones²⁰ 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 desilylated 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 telluroles (**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*-vinyltelluroles (**16**). However, this possibility was eliminated by the facts that the regio isomers, *E*-vinyltelluroles (**17**), which might not cyclize to form the tellu-

razepines (**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 reported²⁵ 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 tellurole 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 propiolanilide.

In order to introduce the conjugated double bond, the lactams (**14b—e**) were treated with trimethyloxonium tetrafluoroborate (Me₃O⁺ BF₄⁻) 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 thiepinines, selenepines and benzotellurazepines¹³ 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-benzotellurazepinene rings using **14** and **18** for comparison with the 1-benzotellurazepines,¹³ whose reactivity was described in our previous report. However, the halogenation with SO₂Cl₂, Br₂ or I₂ 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 (<i>m/z</i> : <i>M</i> ⁺)	IR cm ⁻¹	¹ H-NMR (500 MHz, <i>J</i> =Hz)			
			3-H	NH	Ph-H	R-H
14a R=Me	C ₁₀ H ₉ NOTe (289)	3176 (NH) 1646 (C=O)	6.54 (q, <i>J</i> =1.8)	9.39 (br s)	7.07 (1H, dd, <i>J</i> =7.3, 7.8) 7.26 (1H, <i>J</i> =7.8) 7.35 (1H, dd, <i>J</i> =7.3, 7.8) 7.80 (1H, d, <i>J</i> =7.8)	2.48 (3H, d, <i>J</i> =1.8) Me
14b R= <i>n</i> -Bu	C ₁₃ H ₁₅ NOTe (331)	3150 (NH) 1654 (C=O)	6.55 (s)	9.39 (br s)	7.06 (1H, dd, <i>J</i> =7.3, 7.8) 7.26 (1H, d, <i>J</i> =7.8) 7.34 (1H, dd, <i>J</i> =7.3, 7.8) 7.80 (1H, d, <i>J</i> =7.8)	0.89 (3H, t, <i>J</i> =7.3) 1.26—1.33 (2H, m) 1.47—1.51 (2H, m) 2.60 (2H, t, <i>J</i> =7.3) <i>n</i> -Bu
14c R= <i>tert</i> -Bu	C ₁₃ H ₁₅ NOTe (331)	3176 (NH) 1652 (C=O)	6.58 (s)	8.09 (br s)	7.05 (1H, dd, <i>J</i> =7.3, 7.8) 7.16 (1H, d, <i>J</i> =7.8) 7.36 (1H, dd, <i>J</i> =7.3, 7.8) 7.87 (1H, d, <i>J</i> =7.8)	1.18 (9H, s) <i>tert</i> -Bu
14d R= <i>n</i> -Hex	C ₁₅ H ₁₉ NOTe (359)	3162 (NH) 1627 (C=O)	6.54 (s)	9.03 (br s)	7.06 (1H, dd, <i>J</i> =7.3, 7.8) 7.24 (1H, d, <i>J</i> =7.8) 7.35 (1H, dd, <i>J</i> =7.3, 7.8) 7.80 (1H, d, <i>J</i> =7.8)	0.86 (3H, t, <i>J</i> =7.3) 1.25—1.29 (6H, m) 1.48—1.52 (2H, m) 2.59 (2H, <i>J</i> =7.3) <i>n</i> -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, <i>J</i> =7.3, 7.5), 6.97 (1H, d, <i>J</i> =7.5), 7.18 (1H, dd, <i>J</i> =7.3, 7.3), 7.28—7.32 (2H, m), 7.37 (1H, d, <i>J</i> =7.5), 7.39—7.743 (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, <i>J</i> =8.0) 6.94 (1H, dd, <i>J</i> =7.7, 7.7) 7.18 (1H, dd, <i>J</i> =8.0, 7.7) 7.44 (1H, d, <i>J</i> =7.7)	0.24 (9H, s) TMS

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. ¹H-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 CDCl₃ using tetramethylsilane as internal standard; *J* values are given in Hz. ¹³C-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 (MgSO₄). 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*-Iodopropylanilides (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% H₂SO₄ (150 ml×2), satd. NaHCO₃ (100 ml×2) and brine (150 ml×2), and dried (MgSO₄). 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). ¹H-NMR (90 MHz, CDCl₃) 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 C₁₀H₈NOI: 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). ¹H-NMR (90 MHz, CDCl₃) 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 C₁₃H₁₄NOI: 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). ¹H-NMR (90 MHz, CDCl₃) 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 C₁₃H₁₄NOI: 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 $\equiv$ C), 1640 (C=O). $^1\text{H-NMR}$ (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, brd, $J=8$ Hz, Ph-H), 7.9–8.5 (1H, br, NH). MS m/z : 355 (M^+ , 28), 228 (100), 219 (20). *Anal.* Calcd for $\text{C}_{15}\text{H}_{18}\text{NOI}$: 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 $\equiv$ C), 1630 (C=O). $^1\text{H-NMR}$ (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, brd, $J=8$ Hz, Ph-H), 8.0 (1H, br, NH). MS m/z : 347 (M^+ , 18), 220 (99), 129 (100). *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{NOI}$: 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 $\equiv$ C), 1642 (C=O). $^1\text{H-NMR}$ (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, brd, $J=8$ Hz, Ph-H), 7.9 (1H, br, NH). MS m/z : 343 (M^+ , 20), 216 (100), 125 (22), 97 (19). *Anal.* Calcd for $\text{C}_{12}\text{H}_{14}\text{NOISi}$: 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 $\times$ 3). The extracts were washed with water (100 ml $\times$ 3), brine (50 ml $\times$ 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 Table 1, HR-MS, IR and $^1\text{H-NMR}$ spectral data for **14** are listed in Table 2.

14a (R=Me): HR-MS m/z : 288.9850 (Calcd for $\text{C}_{10}\text{H}_9\text{NOTe}$: 288.9746). $^{13}\text{C-NMR}$ (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 $\text{C}_{13}\text{H}_{15}\text{NOTe}$: C, 47.48; H, 4.60; N, 4.26. Found: C, 47.49; H, 4.54; N, 4.25. $^{13}\text{C-NMR}$ (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 $\text{C}_{13}\text{H}_{15}\text{NOTe}$: C, 47.48; H, 4.60; N, 4.26. Found: C, 47.68; H, 4.64; N, 4.12. $^{13}\text{C-NMR}$ (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 $\text{C}_{15}\text{H}_{19}\text{NOTe}$: C, 50.48; H, 5.37; N, 3.92. Found: C, 50.43; H, 5.27; N, 3.95. $^{13}\text{C-NMR}$ (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 $\text{C}_{15}\text{H}_{11}\text{NOTe}$: 350.9903). $^{13}\text{C-NMR}$ (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 $\text{C}_{12}\text{H}_{15}\text{NOSiTe}$: 346.9985).

Treatment of 14 with $\text{Me}_3\text{O}^+ \text{BF}_4^-$: 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 $\text{Me}_3\text{O}^+ \text{BF}_4^-$ (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 $\times$ 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. $^1\text{H-NMR}$ (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 $\text{C}_{14}\text{H}_{17}\text{NOTe}$: 345.0372).

18c (R=*tert*-Bu): 31 mg, 45% yield, colorless oil. $^1\text{H-NMR}$ (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 $\text{C}_{14}\text{H}_{17}\text{NOTe}$: 345.0372).

18d (R=*n*-Hex): 29 mg, 40% yield, colorless oil. $^1\text{H-NMR}$ (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 $\text{C}_{16}\text{H}_{21}\text{NOTe}$: 373.0685).

18d (R=Ph): 28 mg, 39% yield, colorless oil. $^1\text{H-NMR}$ (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 $\text{C}_{16}\text{H}_{13}\text{NOTe}$: 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. $^1\text{H-NMR}$ (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 $\text{C}_{14}\text{H}_{17}\text{NO}$: 215.1310).

4-*tert*-Butyl-2-methoxyquinoline (19c): 7.5 mg, 87% yield, colorless oil. $^1\text{H-NMR}$ (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 $\text{C}_{14}\text{H}_{17}\text{NO}$: 215.1310).

4-*n*-Hexyl-2-methoxyquinoline (19d): 6.5 mg, 67% yield, colorless oil. $^1\text{H-NMR}$ (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 $\text{C}_{16}\text{H}_{21}\text{NO}$: 243.1623).

Acknowledgements A part of his work was supported by a Grant-in-Aid for Scientific Research from The Ministry of Education, Culture, Sports, Science and Technology of Japan, and The Specific Research Fund of Hokuriku University. The authors wish to express appreciation to Mr. K. Tashiro and Miss H. Kubo for their technical support and to Mr. M. Teranishi for the $^{13}\text{C-NMR}$ measurement.

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