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Δ^3-1,3,4-Telluradiazolines, a Novel Tellurium Containing Heterocycle: One-pot Synthesis, Structure, and Reactivity

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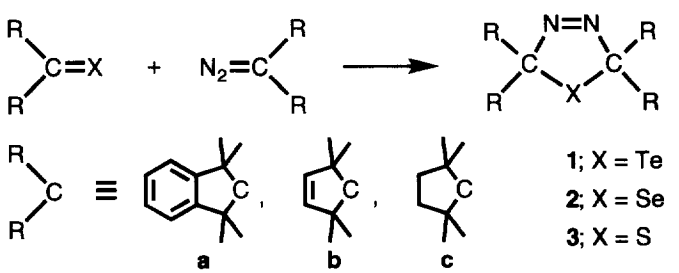
Abstract: The one-pot reaction of sterically hindered hydrazones with tellurium dichloride or tellurium tetrahalide in the presence of triethylamine in benzene afforded Δ^3-1,3,4-telluradiazolines **1**, a novel heterocycle, via 1,3-dipolar cycloaddition of telluroketones and diazo compounds, both generated *in situ*. The molecular structure of **1a** was established by X-ray crystallographic analysis. The photolysis of **1a** led to instant and quantitative formation of the corresponding azine **8a**, whereas the thermolysis of **1a** in the solid state afforded the corresponding retrocyclization products.

As a result of increasing importance of tellurium reagents in organic synthesis,[1] organotellurium chemistry[1, 2] including that of tellurium-containing heterocycles[3] has been developed in the last two decades. Although many sulfur and/or selenium-containing heterocyclic systems have been known in the literature, the corresponding tellurium analogues have been still unknown in many cases.[3]

The carbon-chalcogen double bond compounds have been useful for the formation of chalcogen-containing heterocycles via cycloadditions such as Diels-Alder reaction and 1,3-dipolar cycloadditions.[4] The chemistry of Δ^3-1,3,4-thia-[5] and selenadiazolines,[6] which can be synthesized by cycloaddition of diazo compounds with the corresponding thio- and selenoketones respectively, has been studied intensively because of their usefulness in the preparation of intriguing molecules such as extremely sterically hindered olefins via thermal two-fold extrusion reactions.[7] However, Δ^3-1,3,4-telluradiazoline **1** can not be synthesized via the cycloaddition route since no stable telluroketone had been known until our recent reports.[8, 9]



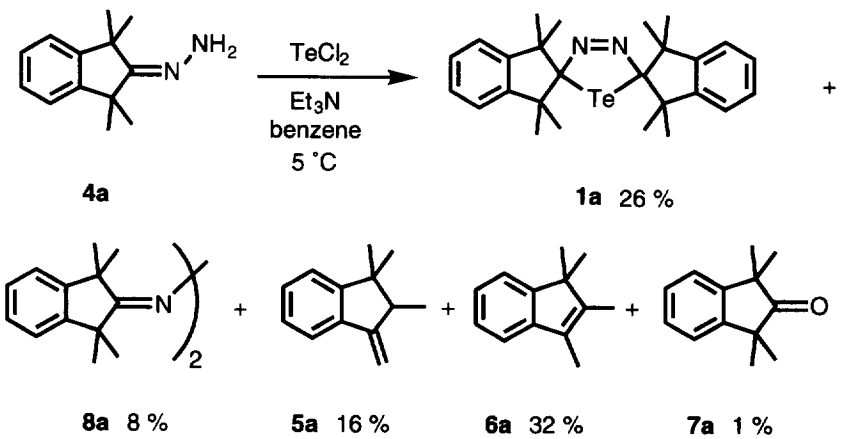
We report here the synthesis of a novel class of heterocycles, Δ^3-1,3,4-telluradiazolines, by the reaction of the corresponding hydrazones with tellurium dichloride.[10] An improved one-pot synthesis by use of tellurium tetrahalide, X-ray crystallographic analysis, and reactivity of the heterocycles are also described.

RESULTS AND DISCUSSIONS

The most widely used method for preparation of sterically protected stable thio-[11] or selenoketones[12] involves reaction of the corresponding hydrazones with sulfur chloride (S_2Cl_2) or selenium halides (Se_2Cl_2 or Se_2Br_2) in the presence of triethylamine.

Since the corresponding tellurium reagent, i.e., tellurium chloride (Te_2Cl_2), is unknown[13] unfortunately, we investigated an analogous telluration reaction by use of tellurium dichloride ($TeCl_2$) in the first stage. No attention has been paid to $TeCl_2$[14] as a tellurating reagent because it is extremely hygroscopic and undergoes ready disproportionation to tellurium and tellurium tetrachloride.

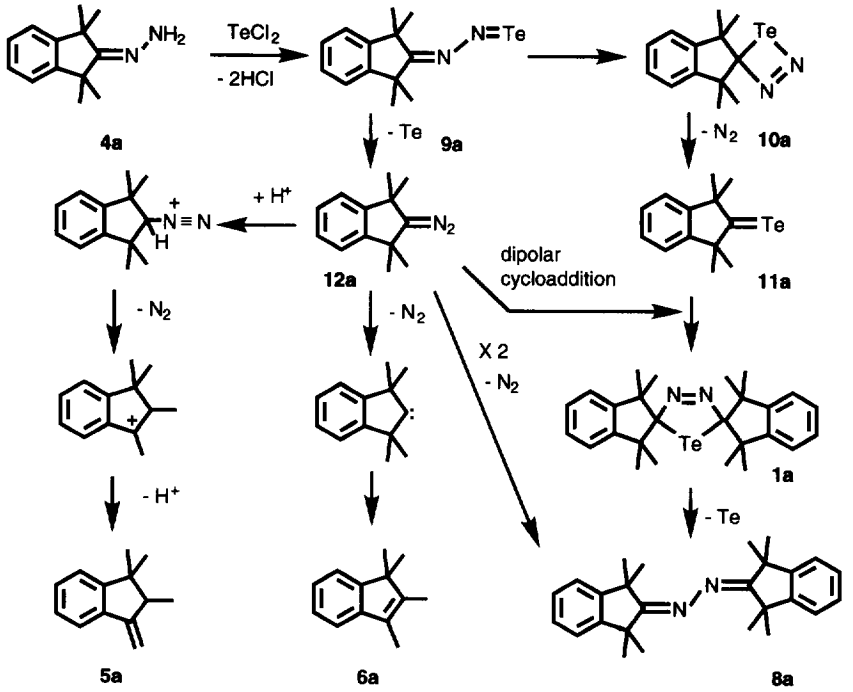
Synthesis of Δ^3-1,3,4-telluradiazolines. The synthesis of telluradiazolines **1** was achieved by reaction of hydrazones **4** with $TeCl_2$ in the presence of triethylamine. To a degassed benzene solution of **4a** (1.00 mmol) and triethylamine (2.40 mmol) was added $TeCl_2$ (1.20 mmol) at 5 °C. After stirring for 1 h, insoluble materials were filtered off through a plug of Celite, the solvent was removed, and the solid residue was washed with pentane carefully to afforded **1a** in 26% yield. The pentane-soluble byproducts were separated by column chromatography to give olefins **5a** (16%) and **6a** (32%), ketone **7a** (1%), and azine **8a** (8%) (Scheme 1).



Scheme 1.

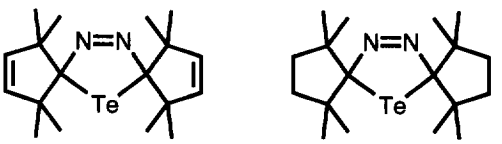
The mechanism of the formation of **1a** is intriguing (Scheme 2). Presumably, a nucleophilic attack of the hydrazone on $TeCl_2$ followed by elimination of hydrogen chloride affords an intermediate *N*-telluronitorosoimine **9a**. The unstable **9a** cyclizes into 1,2,3-telluradiazete **10a**, which extrudes nitrogen to give telluroketone **11a**. On the other hand, detelluration of **9a** gives a diazo compound **12a**. Telluradiazoline

1a is most likely formed by 1,3-dipolar cycloaddition of telluroketone **11a** with the diazo compound **12a**, both generated in situ, as shown in the Scheme 2. The other products **5a**, **6a**, and **8a** are produced by decomposition reaction of **12a**, and ketone **7a** seems to be formed by oxidation of telluroketone **11a** during the work-up procedure.



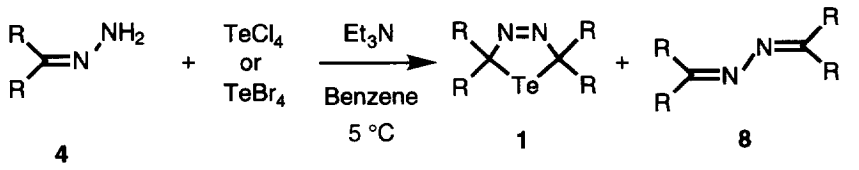
Scheme 2.

Telluradiazolines **1b** (10%) and **1c** (11%) were similarly synthesized from the corresponding hydrazones. Since compounds **1b** and **1c** were soluble in pentane, these were purified by column chromatography (silica gel/hexane), unlike **1a** which was purified by recrystallization. The poorer yields for **1b** and **1c** than that for **1a** are due to their lower stability in chromatography.



1b **1c**

Since $TeCl_2$ is difficult to handle as mentioned above, it is synthetically useful if commercially available and stable tellurium tetrahalides (TeX_4) can be used instead of $TeCl_2$. In fact, use of tellurium tetrachloride ($TeCl_4$) or tellurium tetrabromide ($TeBr_4$) gave telluradiazolines **1a-c** along with azines **8a-c** as a sole by-product, respectively (Scheme 3 and Table 1).

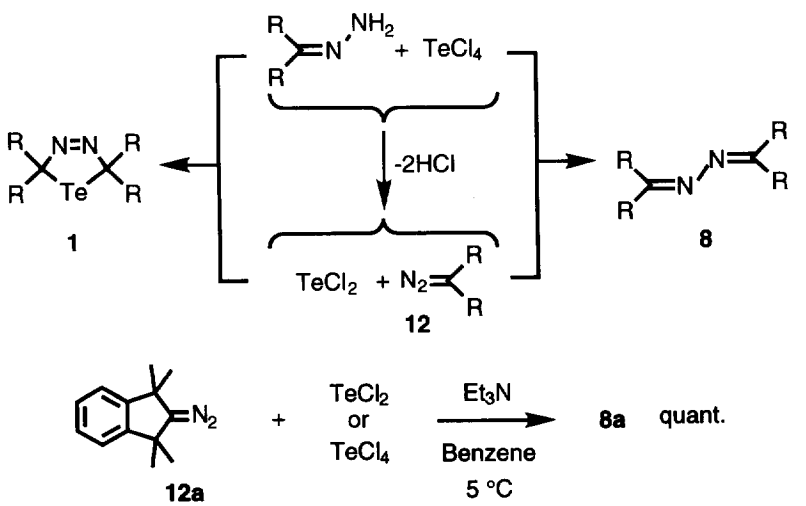


Scheme 3.

Table 1. Yields of Telluradiazolines **1** by the Reaction of Hydrazone **4** with Tellurium Tetrahalide

Hydrazone	Tellurium tetrahalide	Products yields / %			
4a	$TeCl_4$	**1a**	48	**8a**	45
	$TeBr_4$		42		44
4b	$TeCl_4$	**1b**	36	**8b**	40
	$TeBr_4$		55		42
4c	$TeCl_4$	**1c**	19	**8c**	32
	$TeBr_4$		46		40

The one-pot reactions of tellurium tetrahalide with hydrazones provide a useful route to **1** in viewpoint of better yields and easier handling of the tellurium reagents than the $TeCl_2$ method. The difference in the yields among the tellurating agent $TeCl_2$, $TeCl_4$, and $TeBr_4$ may reflect the apparent difference in stability of these reagents. In the reactions using $TeCl_4$ or $TeBr_4$, the corresponding divalent species ($TeCl_2$ or $TeBr_2$) is considered to be formed *in situ* as reactive species, and probably they are much more efficient reagents than $TeCl_2$ prepared beforehand (Scheme 4).



Scheme 4.

The formation of azine **8a** in the TeX_4 method is most likely explained in terms of the reaction of the diazo compound **12a** with $TeCl_2$ or $TeCl_4$, because separate experiments showed that the reaction of **12a** with $TeCl_2$ or $TeCl_4$ in the presence of triethylamine afforded the corresponding azine **8a** quantitatively although the mechanism is not clear at present.

Spectroscopic and structural properties of 1. Telluradiazolines **1a-c** are pale yellow and thermally stable crystalline compounds, though they are highly light-sensitive even in the solid state (*vide infra*).

In the UV spectra of the 1,3,4-chalcogenadiazolines, [**1a**, 340 (ε 640); **2a**, 306 (750); **3a**, 282 nm (1100)], the absorption of the tellurium analogue **1a** is most red-shifted with the smallest molar extinction coefficient. The ^{13}C NMR spectra of **1a-c** show the chemical shifts of the spiro carbons (**1a**, 133.2; **1b**, 128.7, **1c**, 130.0 ppm) which are relatively downfield shifted compared with those of the corresponding selenadiazoline **2a** (131.1 ppm)[6f] and thiadiazoline **3a** (128.4 ppm).[5e] In ^{125}Te NMR spectra, telluradiazolines **1a-c** resonate at much higher field (δ_{Te}:**1a**, -196.6; **1b**, -217.0; **1c**, -144.0) than those expected for tellurides (ca. 0 – 800 ppm).[15] This is obviously due to the shielding effect of the nitrogen-nitrogen double bond nearby the tellurium nucleus.

The molecular structure of the novel heterocyclic compound **1a** was determined by X-ray crystallographic analysis. The molecular structure and crystal packing plot are shown in Figures 1 and 2, respectively. The bond lengths and bond angles of **1a** are listed in Tables 2 and 3, respectively. The 1,3,4-telluradiazoline ring in **1a** is planar and approximately perpendicular to the indan rings. The bond angle of C-Te-C (82.6°) is slightly smaller than those of the reported tellurium-containing five-membered systems,[4,16] while the bond lengths are normal. Although it is well known that organotellurium hetreocycles containing nitrogen atom(s) can be stabilized by intermolecular Te-N interactions,[17] as exemplified by 1,2-benzotellurazole (2.46 Å)[18] and 1,2,5-telluradiazole (2.76 Å),[19] no such significant interaction around the tellurium is observed in **1a** (Figure 2), where the intermolecular Te-N distance is 3.43 Å.

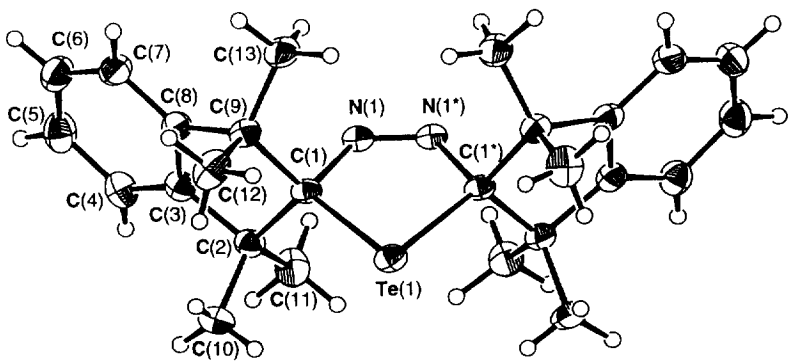


Figure 1. ORTEP drawing of telluradiazoline **1a** with thermal ellipsoid plots (30% probability).

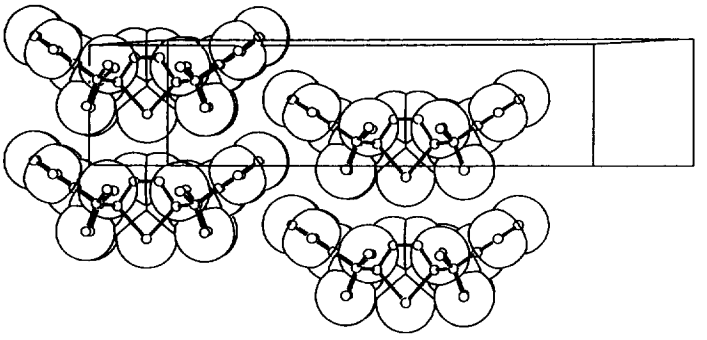


Figure 2. Packing plot of **1a**.

Table 2. Bond Lengths (Å) for **1a**

Te(1)–C(1)	2.178(2)	C(3)–C(4)	1.394(4)
Te(1)–C(1*)	2.178(2)	C(3)–C(8)	1.379(3)
N(1)–N(1*)	1.227(4)	C(4)–C(5)	1.385(4)
N(1)–C(1)	1.486(3)	C(5)–C(6)	1.373(5)
C(1)–C(2)	1.590(4)	C(6)–C(7)	1.384(5)
C(1)–C(9)	1.589(2)	C(7)–C(8)	1.391(3)
C(2)–C(3)	1.511(3)	C(8)–C(9)	1.517(4)
C(2)–C(10)	1.543(4)	C(9)–C(12)	1.540(4)
C(2)–C(11)	1.528(3)	C(9)–C(13)	1.528(4)

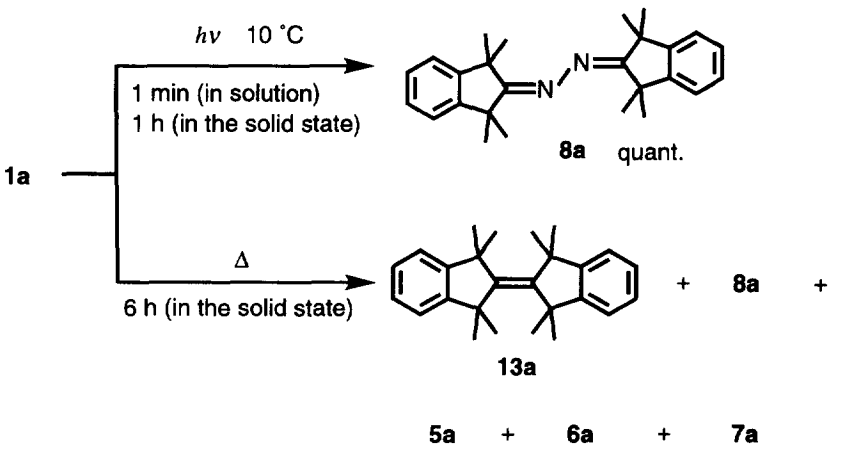
Table 3. Bond Angles (deg) for **1a**

C(1)–Te(1)–C(1*)	82.6(1)	C(2)–C(3)–C(8)	112.0(2)
N(1)–N(1*)–C(1)	123.7(1)	C(4)–C(3)–C(8)	120.1(2)
Te(1)–C(1)–N(1)	105.0(1)	C(3)–C(4)–C(5)	119.2(3)
Te(1)–C(1)–C(2)	116.4(1)	C(4)–C(5)–C(6)	120.4(3)
Te(1)–C(1)–C(9)	116.8(1)	C(5)–C(6)–C(7)	120.8(2)
N(1)–C(1)–C(2)	107.0(2)	C(6)–C(7)–C(8)	119.1(3)
N(1)–C(1)–C(9)	106.4(2)	C(3)–C(8)–C(7)	120.4(3)
C(2)–C(1)–C(9)	104.5(2)	C(3)–C(8)–C(9)	112.0(2)
C(1)–C(2)–C(3)	101.5(2)	C(7)–C(8)–C(9)	127.7(2)
C(1)–C(2)–C(10)	112.7(2)	C(1)–C(9)–C(8)	101.5(2)
C(1)–C(2)–C(11)	113.4(2)	C(1)–C(9)–C(12)	113.1(2)
C(3)–C(2)–C(10)	109.2(2)	C(1)–C(9)–C(13)	113.6(2)
C(3)–C(2)–C(11)	112.4(2)	C(8)–C(9)–C(12)	109.7(2)
C(10)–C(2)–C(11)	107.6(2)	C(8)–C(9)–C(13)	111.4(2)
C(2)–C(3)–C(4)	127.8(2)	C(12)–C(9)–C(13)	107.4(2)

Reactivities of 1a. In general, tellurium (II) containing heterocycles can be easily converted to the corresponding dihalogenated tellurium (IV) compounds,[20] but the reaction of telluradiazoline **1a** with bromine or iodine gave the corresponding azine **8a** quantitatively. Presumably, **1a** reacts with halogen to give the dihalogenated compound, which readily undergoes extrusion of tellurium dihalide to produce azine **8a**.

Since telluradiazolines **1a-c** are extremely light sensitive, the photochemical behavior of **1a** was investigated. When telluradiazoline **1a** in benzene was photolyzed by a 100 W medium pressure Hg lamp through Pyrex at 20 °C, immediate extrusion of tellurium took place to give the corresponding azine **8a** quantitatively (Scheme 5). Even in the solid state, **1a** extruded tellurium during 1 h upon irradiation. The photolysis of selenadiazoline **2a** proceeded, though slowly, to afford **8a** as in the case of **1a**. The fact that **1a** is more reactive than the corresponding selenium analogue **2a** reflects the weakness of the carbon-tellurium bond compared to the carbon-selenium bond.[6g]

The thermolysis of **1a** was performed at 80, 160, and 200 °C in the solid state. Although **1a** was stable at 80 °C for 6 h without any perceptible decomposition, the pyrolysis at 160 and 200 °C afforded the decomposition products **5a**, **6a**, **7a**, **8a**, and **13a** (Scheme 5 and Table 4). On the contrary, pyrolysis of the corresponding selenadiazoline **2a** gave mainly two fold extrusion product **13a**.[6g]



Scheme 5

Table 4. Reaction Products of the Thermolysis of **1a** in the Solid State

	Yield / %				
	13a	**8a**	**5a**	**6a**	**7a**
80 °C		no reaction			
160 °C	27	13	43	108	9
200 °C	15	8	29	144	4

The relatively low yield of the two fold extrusion product **13a** in the reaction of **1a** compared with the thermolysis of **2a** seems to be due to competitive retrocyclization of telluradiazoline **1a** leading to telluroketone **11a** and the diazo compound **12a**, which was previously observed in the thrmolysis of 1a in solution.[8] Both **1a** and **12a** may produce **5a**, **6a**, and **7a**.

EXPERIMENTAL

Melting points were recorded under argon atmosphere on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. IR spectra (KBr disk) were recorded on a Horiba FT-200 spectrometer. UV-vis spectra were taken with a Jasco Ubest-50 spectrometer using 1 cm quartz cells. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AM-500 (500 MHz, 125 MHz), a JEOL α-500 (500 MHz, 125 MHz) or a JEOL EX-270 (270 MHz, 67.5 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane or a residual solvent as an internal standard. DEPT pulse sequences was used for the assignment. ^{125}Te NMR spectra were obtained on a JEOL α-500 (158.0 MHz) or a JEOL EX-270 (85.1 MHz) spectrometer. Chemical shifts were measured relative to Me_2Te (0 ppm) in $CDCl_3$ as an external standard. High resolution mass spectra were obtained with a JEOL JMS-SX102L spectrometer at an ionization potential of 70 eV. For column chromatography, silica gel C-200 (Wako) was employed. Filtration was carried out by using a pad of Celite No.545 (Celite) or Cellulose powder C (Toyo Roshi).

All reactions and manipulations involving tellurium were performed using Schlenck techniques in the dark. Unless otherwise noted, all reactions were performed using oven dried glassware, which was then evacuated and subsequently filled with dry argon. All reactions were carried out under slightly positive pressure of dry argon or degassed atmosphere. Solvents were purified and degassed by a standard procedure.

Tellurium dichloride ($TeCl_2$) was synthesized by the reported method.[21] Tellurium tetrachloride ($TeCl_4$) and tellurium tetrabromide ($TeBr_4$) were purchased from Aldrich Chemical Company, Inc. 2-Indanone,[22] 2,2,5,5-tetramethyl-3-cyclopentenone,[6e] 2,2,5,5-tetramethyl-3-cyclopentanone,[23] 1,1,3,3-tetramethyl-2-indanone hydrazone,[6f] 2,2,5,5-tetramethyl-3-cyclopentenone hydrazone,[6e] 2,2,5,5-tetramethyl-3-cyclopentanone hydrazone[6f] were synthesized by the reported methods.

Preparation of 1,1,3,3-Tetramethyl-2-indanone (7a). A modified Rathke's permethylation method was used.[24] To a suspension of potassium hydride (34.4 g, 0.86 mol) in THF (800 ml) was added a THF solution (80 ml) of 2-indanone (26.4 g, 0.200 mol) dropwise over a 5 min period at 25 °C. After additional stirring for 5 min, to the solution was added dropwise methyl iodide (122 g, 0.86 mol) over 15 min. After an additional stirring for 30 min, the reaction mixture was treated with water (160 ml). The aqueous layer was extracted with ether and the combined organic layers were dried over anhydrous $MgSO_4$. After the solvent was evaporated, the residue was subjected to steam distillation to give **7a** (34.8 g, 0.184 mol, 92.4%); mp 74.5-75.5 °C. The spectra of **7a** were identical with those previously reported.[25]

Synthesis of 1,3,4-Telluradiazolines. General Procedure. a) $TeCl_2$ method. To a benzene solution (20 ml) of triethylamine (243 mg, 2.40 mmol) and hydrazone **4a** (202 mg, 1.00 mmol) was added freshly prepared powdered tellurium dichloride (238 mg, 1.20 mmol) via a bent solid inlet tube at 5 °C, and the mixture was well stirred for 1 h. After dark gray insoluble materials were filtered off through a plug of Celite, the solvent was removed under reduced pressure. The residue was washed carefully with pentane to afford telluradiazoline **1a** (65.2 mg, 26%). Chromatographic separation of pentane-soluble products (silica gel/hexane) gave azine **8a** (8%), olefins **5a** (16%) and **6a** (32%), and ketone **7a** (1%). **b) $TeBr_4$ method.** Tellurium tetrabromide (2.73 g, 6.10 mmol) was added to a stirred benzene solution (60 ml) of triethylamine (1.23 g, 12.2 mmol) and hydrazone **4a** (1.21 g, 6.00 mmol) via a bent solid inlet tube at 5 °C. The color of the solution changed slowly first to light orange, then to dark green, finally to black during the reaction. After the solution was stirred for 2 h at 5 °C, a black-green suspension was obtained. After the dark green insoluble material was filtered off through a plug of Celite, the solvent was removed under reduced pressure. The residue was washed carefully with pentane to afford telluradiazoline **1a** (631 mg, 42%). Chromatographic separation of pentane-soluble products (silica gel/hexane) gave azine **8a** (491 mg, 44%).

$TeCl_4$ can be used instead of $TeBr_4$ in the same procedure. Other telluradiazolines **1b** and **1c** were prepared in a manner similar to that for **1a** from the corresponding hydrazones **4b** and **4c** in both $TeCl_2$ and $TeBr_4$ methods, and their yields are listed in Table 1.

Bis-1,1,3,3-tetramethylindan-2-spiro-2',5'-Δ^3-1',3',4'-telluradiazoline (1a): Pale yellow needles; mp 162-164 °C (decomp); ^{1}H NMR($CDCl_3$, 500 MHz) δ = 1.13(s, 12H), 1.53(s, 12H), 7.21-7.26(m, 8H); ^{13}C NMR($CDCl_3$, 125 MHz) δ = 23.9(q), 37.4(q), 53.8(s), 122.8(d), 127.4(d), 133.2(s), 148.3(s); ^{125}Te NMR($CDCl_3$, 85.1 MHz) δ = −196.6; IR (KBr) 1591, 1577, 1481, 1450, 1376, 1364, 1313, 957, 841 cm^{-1}; UV-vis(cyclohexane) λ_{max} 340 nm (ε 640). HRMS (70 eV) found: *m/z* 502.1641; calcd for $C_{26}H_{32}N_2{}^{130}Te$: M, 502.1628. Found: C, 62.15; H, 6.22; N, 5.47%. Calcd for $C_{26}H_{32}N_2Te$: C, 62.44; H, 6.45; N, 5.60%.

Bis-2,2,5,5-tetramethylcyclopentene-spiro-2',5'-Δ^3-1',3',4'-telluradiazoline (1b): pale yellow needles, mp 115-117 °C (decomp); ^{1}H NMR($CDCl_3$, 500 MHz) δ = 0.83(s, 12H), 1.30(s, 12H), 5.79(s, 4H); ^{13}C NMR($CDCl_3$, 125 MHz) δ = 23.4(q), 34.9(q), 55.8(s), 128.7(s), 137.5(d); ^{125}Te NMR($CDCl_3$, 85.1 MHz) δ = −217.0. HRMS (70 eV) found: *m/z* 402.1333.; calcd for $C_{18}H_{28}N_2{}^{130}Te$: M, 402.1324.

Bis-2,2,5,5-tetramethylcyclopentane-spiro-2',5'-Δ^3-1',3',4'-telluradiazoline (1c): pale yellow needles, mp 108-110 °C (decomp); ^{1}H NMR($CDCl_3$, 500 MHz) δ = 0.78(s, 12H), 1.23(s, 12H), 1.91-2.20(AA'BB', 8H); ^{13}C NMR($CDCl_3$, 125 MHz) δ = 26.8(q), 35.9(q), 39.1(t), 50.8(s), 130.0(s); ^{125}Te NMR($CDCl_3$, 85.1 MHz) δ = −144.0. HRMS (70 eV) found: *m/z* 406.1625.; calcd for $C_{18}H_{32}N_2{}^{130}Te$: M, 406.1627.

X-ray Crystallographic Analysis of 1a: The diffraction-quality single crystals of **1a** were obtained by the slow evaporation of a saturated solution in dichlorometane and hexane (1:1) in the dark at room temperature. The intensity data ($2\theta < 55°$) were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71609 Å) and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was

based on 2356 observed reflections [$I > 3.00\sigma(I)$] and 196 variable parameters with $R(R_w) = 0.025(0.033)$. Crystal data for **1a**; $C_{26}H_{32}N_2Te$, FW = 500.15, monoclinic, space group $C2/c$, a = 25.806(5), b = 6.2511(3), c = 15.608(4) Å, β = 114.28(1)°, V = 2294(1) Å^3, Z = 4, D_c= 1.447 g cm^{-3}, μ = 13.11 cm^{-1}, F(000)=1016. The final values of selected bond lengths and angles are listed in Tables 2 and 3. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ(UK), on quoting the full journal citation.

Reaction of 2-Diazo-1,1,3,3-tetramethylindan (12a) with $TeCl_2$: To a benzene solution (7 ml) of triethylamine (170 mg, 1.68 mmol) and **12a** (140 mg, 0.700 mmol) was added freshly prepared powdered $TeCl_2$ (167 mg, 0.84 mmol) via a bent solid inlet tube at 5 °C, and the mixture was well stirred for 1 h. After insoluble materials were filtered off through a plug of Celite, the filtrate was washed with water and the solvent was removed under reduced pressure. The residue was chromatographed to give azine **8a** (111 mg, 85%).

Reaction of Telluradiazoline 1a with Bromine. To a stirred solution of **1a** (100 mg, 0.200 mmol) in dichrolomethane (10 ml) was added a carbon tetrachloride solution (1 ml) of bromine (31.9 mg, 0.200 mmol) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 1 h. After insoluble substances were filtered off through a plug of Cellulose powder, the solvent was removed under reduced pressure. The residue was chromatographed to give azine **8a** (74.0 mg, 99%).

Photolysis of Telluradiazoline 1a. A C_6D_6 (0.5 ml) solution of telluradiazoline **1a** (5 mg) in a sealed Pyrex NMR tube with 4 mm inside diameter and 0.5 mm wall was photolyzed by a medium pressure 100 W Hg lamp at 5 °C for 1 min. Only the corresponding azine **8a** was observed by ^{1}H NMR.

Solid State Thermolysis of Telluradiazoline 1a. General Procedures. The telluradiazoline **1a** (25 mg) in a sealed tube was heated at 160 °C for 6 h. To the cooled reaction mixture was added $CDCl_3$ and an NMR spectrum (500 MHz) of the solution was taken. The peak area (2.1-0.9 ppm) was integrated to determine the product distribution by comparison with authentic samples. The results are listed in Table 4.

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