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Synthesis of Δ^3-1,3,4-Telluradiazolines, a Novel Tellurium-Containing Heterocycle

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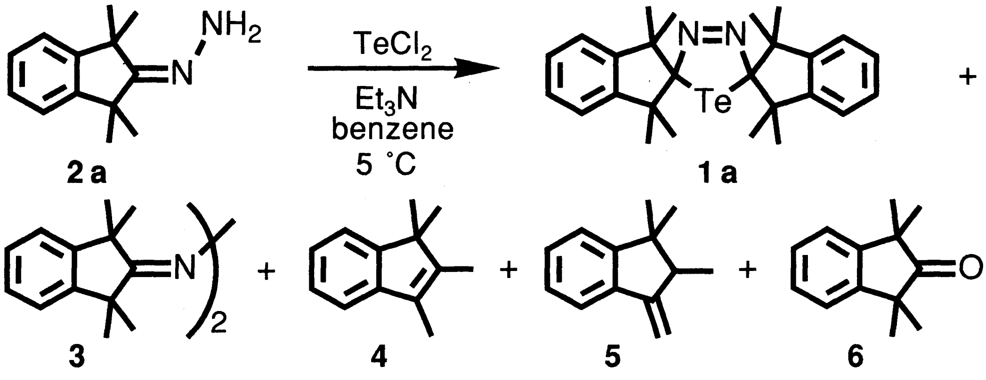
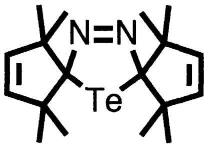
Reaction of sterically hindered hydrazones with tellurium dichloride in the presence of triethylamine in benzene afforded Δ^3-1,3,4-telluradiazolines, a novel heterocycle, probably via 1,3-dipolar cycloaddition of telluroketones with diazo compounds, both generated in situ.

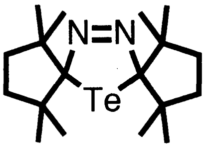
The chemistry of Δ^3-1,3,4-thia-1) and selenadiazolines,2) which can be synthesized by cycloaddition of diazo compounds with corresponding thio- and selenoketones respectively, have intensively been studied because of their usefulness in the preparation of intriguing molecules such as extremely sterically hindered olefins by thermal two-fold extrusion reactions.1,2) It is known that the selenadiazolines are more useful than the thiadiazolines in the two-fold extrusion methodology because of the greater magnitude of the atomic radius of selenium.2a) It is reasonably considered, therefore, that the tellurium analogue, Δ^3-1,3,4-telluradiazoline, is more suitable, but the cycloaddition route to the telluradiazoline is impossible since no stable telluroketone has been known.3) We now describe here the first synthesis of a novel heterocycle, Δ^3-1,3,4-telluradiazoline **1**, by a unique reaction of a hydrazone with tellurium dichloride.

Treatment of 1,1,3,3-tetramethylindanone hydrazone (**2a**)2b) with tellurium dichloride4) in the presence of triethylamine gave telluradiazoline **1a** in 26% yield. A typical procedure for the preparation of **1a** follows. To a degassed benzene solution (20 ml) of triethylamine (243 mg, 2.40 mmol) and hydrazone **2a** (202 mg, 1.00 mmol) was added freshly prepared powdered tellurium dichloride (238 mg, 1.20 mmol) at 5 °C under an argon atmosphere in the dark, and the mixture was well stirred for 1 h. After the insoluble material was filtered off through a plug of Celite, the solvent was removed under reduced pressure. The residue was washed with pentane carefully to afford **1a** (65.2 mg, 26%).5) Chromatographic separation of pentane-soluble products (silica gel/hexane) gave azine **3** (8%), olefins **4** (32%) and **5** (16%), and ketone **6** (1%).





1b

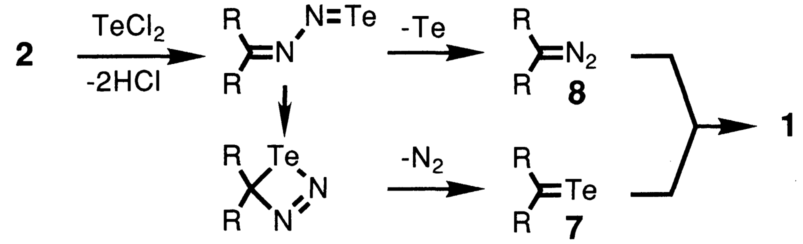


1c

Telluradiazolines **1b** (10%) and **1c** (11%) were similarly synthesized from the corresponding hydrazones.[5,6] Telluradiazolines **1a-c** are thermally stable crystalline compounds though highly light sensitive even in the solid state. The spectral characteristic of **1** is considerably low chemical shifts of the spiro carbons in their ^{13}C-NMR spectra (133.2(**1a**), 128.7(**1b**), 130.0(**1c**)), which are shifted downfield compared with those of the corresponding thia-[1c] and selenadiazolines.[2b,c]

Telluradiazolines **1** are most likely formed by 1,3-dipolar cycloaddition of telluroketone **7** with diazo compound **8**, both generated in situ, as shown in the following scheme. We previously reported similar reactions of hydrazones with sulfur chloride or selenium chloride resulting in the synthesis of stable thio- or selenoketones.[7]

Further investigation on the reactivities of these novel telluradiazolines **1** is currently in progress.



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5) **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 $C_{26}H_{32}N_2{}^{130}Te$: 502.1628. **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); HRMS (70 eV): Found: *m/z* 402.1333. Calcd for $C_{18}H_{28}N_2{}^{130}Te$: 402.1324. **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); HRMS (70 eV): Found: *m/z* 406.1625. Calcd for $C_{18}H_{32}N_2{}^{130}Te$: 406.1627.

6) Compounds **1b** and **1c** were purified by column chromatography (silica gel/hexane). The lower yields for **1b** and **1c** than for **1a** are due to their decomposition during the chromatography.

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