

Synthesis of Δ^4 -1,2,4-Thiatellurazolines

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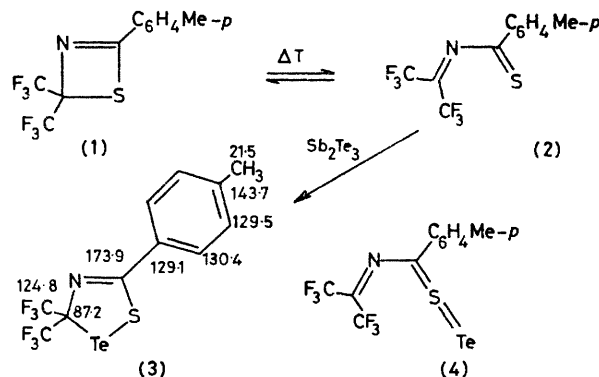
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Summary The synthesis of Δ^4 -1,2,4-thiatellurazolines (3), the first S, Te, and N containing heterocyclic system, from 2*H*-1,3-thiazetes (1) is described.

THE number of heterocyclic systems known which contain tellurium together with other heteroatoms in the same ring is rather small.^{1,2} We now report access to the hitherto undescribed Δ^4 -1,2,4-thiatellurazoline system (3).

2*H*-1,3-Thiazetes (1) above *ca.* 80 °C exist in a thermally mobile equilibrium with the synthetically valuable 1,3-thiazabuta-1,3-dienes (2).^{3,4} On heating compound (1) in the presence of 1 mol. equiv. of finely ground antimony(III) telluride at 80–90 °C for 4–5 weeks in toluene in the dark, compound (3) (m.p. 72–73 °C)[†] was obtained in 15%

[†] Satisfactory C, H, and N analyses were obtained ($\pm 0.1\%$).



yield as brown-red crystals after column chromatography (silica gel-hexane). Compound (1) reacts similarly with indium(III) telluride and with elemental tellurium, but the yields are lower.

The structural assignment is based on spectroscopic data: i.r. (KBr) 1607 and 1594 cm^{-1} ; ^1H n.m.r. (CCl_4 ; SiMe_4) δ 2.48 (s, 3H), 7.15–7.45 (m, 2H), and 7.91–8.20 (m, 2H); ^{19}F n.m.r. δ (CCl₄) δ -9.7 p.p.m. (s, 6F). The ring-opened structure (4) can be ruled out on the basis of ^{13}C n.m.r. data. § The mass spectra showed peaks at m/e 429 (M^+), 360 ($M^+ - \text{CF}_3$), 299 ($M^+ - \text{Te}$), 280 ($M^+ - \text{Te}, -\text{F}$), 267 ($M^+ - \text{Te}, -\text{S}$), 248 ($M^+ - \text{Te}, -\text{S}, -\text{F}$), 230 ($M^+ - \text{Te}, -\text{CF}_3$), 198 ($M^+ - \text{Te}, -\text{S}, -\text{CF}_3$), 135 ($\text{C}_7\text{H}_7\text{CS}^+$), 117 ($\text{C}_7\text{H}_7\text{CN}^+$), and 69 (CF_3^+). The molecular ion-radical

shows the isotopic abundance characteristic of tellurium; $^{126}\text{Te}; ^{128}\text{Te}; ^{130}\text{Te} = 18.7:31.8:34.5$. ¶

The brown-red crystals give violet solutions which are extremely sensitive to light. Compound (3), even below room temperature, reacts with phosphites and multiple bond systems with elimination of tellurium, and therefore may be used as an equivalent for the hetero-1,3-diene (2) at low temperatures for cycloaddition processes.⁵

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‡ Recorded with a Jeol C 60 HL instrument operating at 56.45 MHz; trifluoroacetic acid was used as external standard.

§ Recorded with a Jeol FX 100 instrument in CDCl_3 with SiMe_4 as internal standard. For data see formula (3).

¶ Recorded with a AEI (Manchester) MS 9 spectrometer at 70 eV; the Te containing fragments are based on isotope ^{130}Te .

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⁵ K. Burger, R. Ottlinger, and A. Proksch, unpublished results.