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

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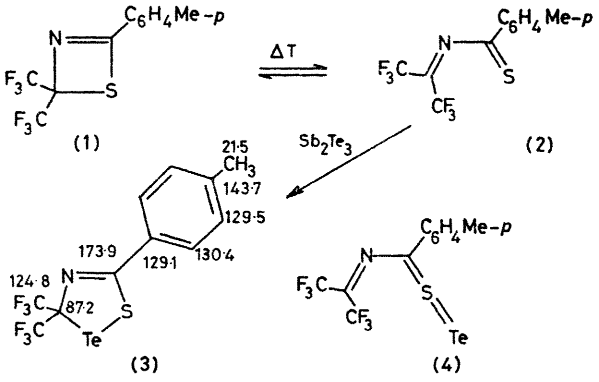
Summary The synthesis of Δ^4-1,2,4-thiatellurazolines (**3**), the first S, Te, and N containing heterocyclic system, from 2*H*-1,3-thiazetes (**1**) is described.

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**).



(1) (2) (3) (4)

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%

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† Satisfactory C, H, and N analyses were obtained (± 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}; ^{1}H 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.‡ (CCl_4) 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 ($M^+ - CF_3$), 299 (M^+ − Te), 280 (M^+ − Te, −F), 267 (M^+ − Te, −S), 248 (M^+ − Te, −S, −F), 230 (M^+ − Te, $-CF_3$), 198 (M^+ − Te, −S, $-CF_3$), 135 ($C_7H_7CS^+$), 117 ($C_7H_7CN^+$), and 69 (CF_3^+). The molecular ion-radical shows the isotopic abundance characteristic of tellurium; ^{126}Te : ^{128}Te : ^{130}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.

[1] 'Organic Compounds of Sulphur, Selenium and Tellurium,' ed. D. H. Reid, Specialist Periodical Reports, The Chemical Society, Vols. 1—4.

[2] K. J. Irgolic, 'The Organic Chemistry of Tellurium,' Gordon and Breach, New York, 1974.

[3] K. Burger, J. Albanbauer, and M. Eggersdorfer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 766; K. Burger, J. Albanbauer, and M. Foag, *ibid.*, p. 767.

[4] K. Burger, R. Ottlinger, and J. Albanbauer, *Chem. Ber.*, 1977, **110**, 2114.

[5] K. Burger, R. Ottlinger, and A. Proksch, unpublished results.