

Structure and Thermolysis of a 1,4,2-Oxatellurazole, a Novel Tellurium Containing Heterocycle

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A novel tellurium containing heterocycle, 1,4,2-oxatellurazole, was characterized by X-ray crystallographic analysis which showed a remarkably small C-Te-C bond angle (79.4°), and its thermolysis afforded the corresponding ketone and isonitrile derived from an intermediary isotellurocyanate in a manner of 1,3-dipolar cycloreversion.

Carbon-chalcogen double bond compounds are known to be useful for the formation of chalcogen containing heterocycles via cycloaddition reactions such as Diels-Alder reaction and 1,3-dipolar cycloaddition in the cases of oxygen, sulfur, and selenium compounds. However, such synthetic routes to tellurium-containing heterocycles have been limited because of instability of the C=Te double bond.¹⁾ Meanwhile, tellurium containing heterocyclic systems are of current interest in heterocyclic chemistry.²⁾ Very recently, we reported the synthesis of the first stable telluroketone **1a** and its application to the synthesis of a novel tellurium-containing heterocycle **2a** by 1,3-dipolar cycloaddition with mesitonitrile oxide (MesCNO).³⁾ Although the corresponding sulfur (1,4,2-oxathiazole)^{4a)} and selenium analogues (1,4,2-oxaselenazole)^{4b)} had been known, **2a** represented the first 1,4,2-oxatellurazole. We now present here the first X-ray structural analysis and interesting thermal behavior of a 1,4,2-oxatellurazole system.

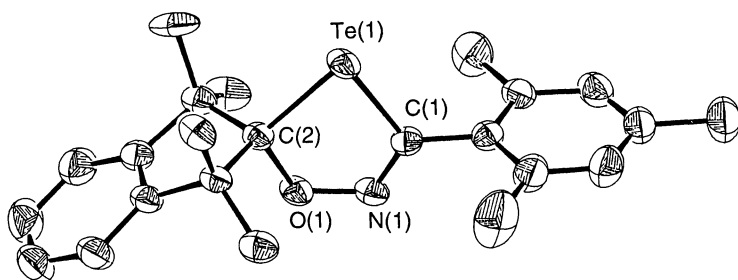
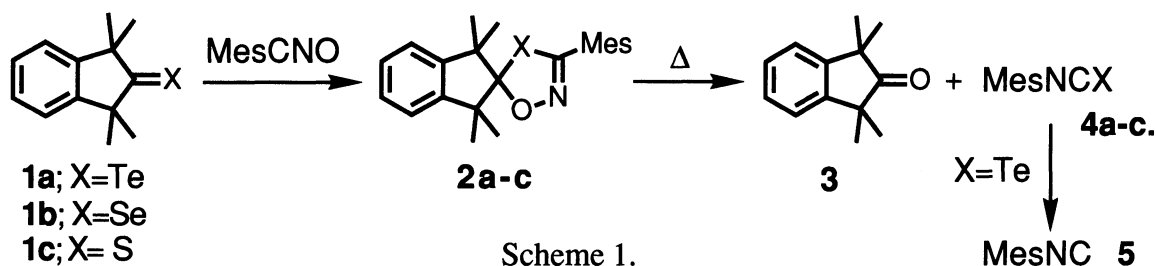


Fig. 1. ORTEP drawing of 1,4,2-oxatellurazole **2a** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles($^\circ$); Te(1)-C(1) 2.105(7), Te(1)-C(2) 2.175(7), C(1)-N(1) 1.264(8), N(1)-O(1) 1.386(8), O(1)-C(2) 1.471(7); C(1)-Te(1)-C(2) $79.4(3)$, Te(1)-C(1)-N(1) $116.8(5)$, C(1)-N(1)-O(1) $117.3(6)$, N(1)-O(1)-C(2) $121.3(5)$, O(1)-C(2)-Te(1) $105.0(4)$.

As shown in Fig. 1,⁵⁾ the oxatellurazole ring of **2a** is almost planar and approximately perpendicular to both of the indan and mesityl rings. Although **2a** has typical bond lengths, the bond angle of C-Te-C (79.4°) is the smallest ever reported for the non-aromatic tellurium five-membered ring systems.⁶⁾

Oxatellurazole **2a** is an extremely light sensitive and thermally unstable compound. The photolysis (medium pressure Hg arc) of **2a** led to instant and quantitative formation of the corresponding ketone **3** and mesitonitrile, whereas the thermolysis of **2a** (in CDCl_3 , 60-90 $^\circ\text{C}$, sealed tube) quantitatively afforded **3** and isonitrile **5** most likely formed from intermediary isotellurocyanate **4a** (Scheme 1). The thermolysis of oxaselenazole **2b**⁷⁾ and oxathiazole **2c**⁷⁾ afforded isoselenocyanate **4b** and isothiocyanate **4c**, respectively, along with **3**.



A kinetic study of the thermolysis of **2a-c** in CDCl_3 using ^1H NMR spectroscopy showed that each reaction was first order in **2**. The rate constants (s^{-1}) were: **2a**; 4.02×10^{-4} (90.0°C), 1.35×10^{-4} (80.0°C), 4.81×10^{-5} (70.0°C), 1.55×10^{-5} (60.0°C), **2b**; 3.60×10^{-6} (90.0°C), **2c**; 2.28×10^{-5} (160.0°C). The rate constants increase in the order of $\text{S} < \text{Se} < \text{Te}$, indicating that the bond strength of the C-X bond governed the process of the cycloreversion. The temperature dependence of the rate constants for **2a** led to the estimation of the activation parameters ($\Delta H^\ddagger = 25.3$ kcal/mol, $\Delta S^\ddagger = -4.95$ e.u.), which are reasonable for 1,3-dipolar cycloreversions.⁸⁾

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- 7) Compounds **2b** and **2c** were quantitatively prepared by the 1,3-dipolar cycloaddition reaction of mesitronitrile oxide with the corresponding seleno- and thioketones in chloroform. All new compounds gave satisfactory elemental analyses and spectral data. **2a**: yellow needles, mp $127-129^\circ\text{C}$ (decomp); ^1H NMR(CDCl_3 , 500 MHz) δ 1.44(s, 6H), 1.52(s, 6H), 2.26(s, 3H), 2.34(s, 6H), 6.86(s, 2H), 7.23(s, 4H); ^{13}C NMR(CDCl_3 , 125 MHz) δ 20.3(q), 21.1(q), 23.7(q), 35.2(q), 53.7(s), 123.1(d), 127.3(d), 128.6(d), 129.9(s), 133.9(s), 136.9(s), 138.8(s), 139.7(s), 147.1(s); ^{125}Te NMR(CDCl_3 , 85.3 MHz) δ 542.2; HRMS (35 eV): m/z Found: 461.1136. Calcd for $\text{C}_{23}\text{H}_{27}\text{NO}^{128}\text{Te}$: 461.1138.; HRMS (70 eV): m/z Found: 274.9952. Calcd for $\text{C}_{10}\text{H}_{11}\text{N}^{130}\text{Te}$ ($M - \text{C}_{13}\text{H}_{16}\text{O}$): 274.9954. **2b**: pale yellow needles, mp $142-143^\circ\text{C}$ (decomp); ^1H NMR(CDCl_3 , 500 MHz) δ 1.42(s, 6H), 1.53(s, 6H), 2.27(s, 3H), 2.39(s, 6H), 6.88(s, 2H), 7.22(m, 4H); ^{13}C NMR(CDCl_3 , 125 MHz) δ 20.0(q), 21.1(q), 23.0(q), 32.2(q), 52.1(s), 122.7(d), 125.7(s), 127.4(d), 128.5(d), 129.7(s), 137.3(s), 139.3(s), 147.3(s), 148.6(s); ^{77}Se NMR(CDCl_3 , 51.5 MHz) δ 409.6. **2c**: white needles, mp $147-148^\circ\text{C}$ (decomp); ^1H NMR(CDCl_3 , 500 MHz) δ 1.39(s, 6H), 1.53(s, 6H), 2.27(s, 3H), 2.40(s, 6H), 6.89(s, 2H), 7.21(m, 4H); ^{13}C NMR(CDCl_3 , 125 MHz) δ 19.9(q), 21.1(q), 22.9(q), 30.5(q), 51.6(s), 122.6(d), 123.6(s), 123.7(s), 127.4(d), 128.5(d), 137.7(s), 139.5(s), 147.2(s), 150.6(s).
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