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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.

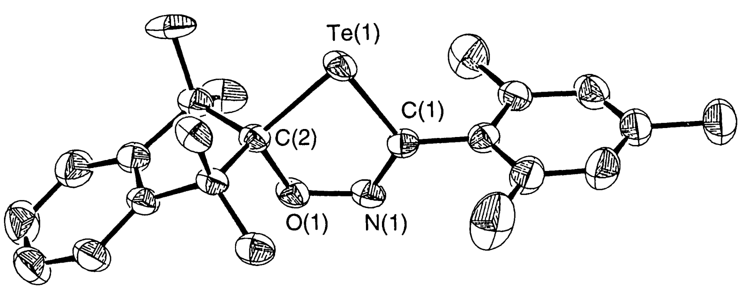
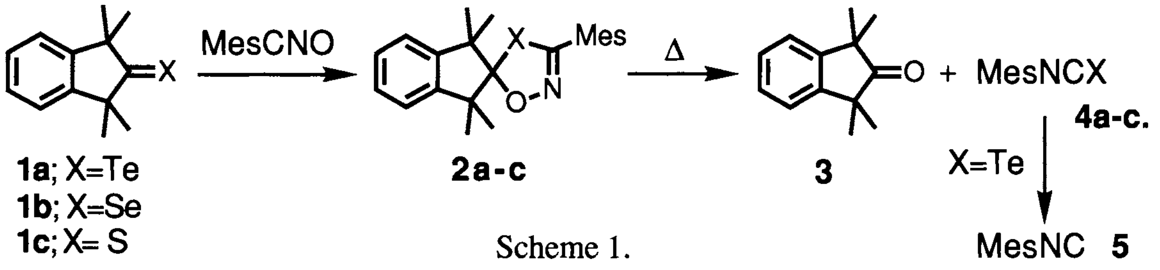


Fig. 1. *ORTEP* drawing of 1,4,2-oxatellurazole **2a** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles(°); Te(1)-C(1) 2.105(7), Te(1)-C(2) 2.175(7), C(1)-N(1) 1.264(8), N(1)-O(1) 1.386(8), O(1)-C(2) 1.471(7); C(1)-Te(1)-C(2) 79.4(3), Te(1)-C(1)-N(1) 116.8(5), C(1)-N(1)-O(1)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



Scheme 1.

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 S<Se<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)]

We thank Dr. N. Tokitoh of the University of Tokyo for the determination of the X-ray structure of **2a**.

References

1) M. R. Bryce, J. Becher, and B. Fält-Hansen, "Advances in Heterocyclic Chemistry," ed by A. R. Katritzky, Academic, New York (1992), Vol. 55, pp. 1; G. Erker and R. Hock, *Angew. Chem., Int. Ed. Engl.*, **28**, 179 (1989); M. Segi, T. Koyama, Y. Tanaka, T. Nakajima, and S. Suga, *J. Am. Chem. Soc.*, **111**, 8749 (1989).
2) I. D. Sadekov, G. M. Abakarov, Y. I. Sadekova, and V. I. Minkin, *Sulfur Rep.*, **6**, 15 (1986); I. D. Sadekov and V. I. Minkin, "Advances in Heterocyclic Chemistry," ed by A. R. Katritzky, Academic, New York (1993), Vol 58, pp. 47.
3) M. Minoura, T. Kawashima, and R. Okazaki, *J. Am. Chem. Soc.*, **115**, 7019 (1993).
4) a) M. P. Sammes, "Comprehensive Heterocyclic Chemistry," ed by C. W. Bird and G. W. H. Chessman, Pergamon, New York, (1984), Vol 6, pp. 897; b) P. T. Meinke and G. A. Krafft, *J. Am. Chem. Soc.*, **110**, 8671 (1988); P. T. Meinke and G. A. Krafft, *ibid.*, **110**, 8679 (1988).
5) Crystallographic data for **2a**: $C_{23}H_{27}NOTe$, M = 461.07, monoclinic, space group $P2_1/c$, a = 12.266(6), b = 11.560(2), c = 15.770(3) Å, β = 100.68(2)°, V = 2197.3(9) $Å^3$, Z = 4, D_c= 1.394 g cm^{-3}, μ = 13.65 cm^{-1}, $R(R_w)$ = 0.064(0.071) for 2980 observed reflection [$I > 3.00\sigma(I)$].
6) I. Hargittai and B. Rozsondai, "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1986), Vol. 1, pp. 63. The smallest C-Te-C angle of 78.6 ° in aromatic five-membered ring systems is reported for 1,3-benzotellurazole. A. E. Mistrukov, I. D. Sadekov, V. S. Sergieno, G. M. Abakarov, M. A. Porai-Koshich, A. A. Shneider, and A. D. Garnovskii, *Khim. Geterotsikl. Soedin.*, **1989**, 1690.
7) Compounds **2b** and **2c** were quantitatively prepared by the 1,3-dipolar cycloaddition reaction of mesitonitrile 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 °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 $C_{23}H_{27}NO^{128}Te$: 461.1138.; HRMS (70 eV): *m/z* Found: 274.9952. Calcd for $C_{10}H_{11}N^{130}Te$ (M - $C_{13}H_{16}O$): 274.9954. **2b**: pale yellow needles, mp 142-143 °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 °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).
8) G. Bianchi and R. Gandolfi "1,3-Dipolar Cycloaddition Chemistry," ed by A. Padwa, Wiley, New York (1984), Vol. 2, pp. 451.

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