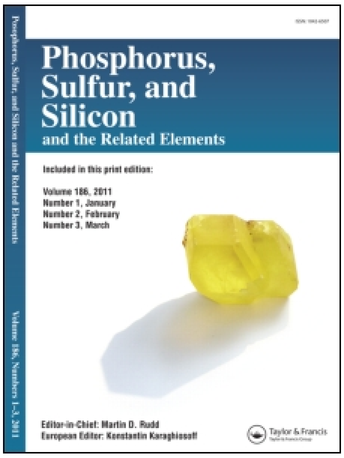

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Synthesis, Structure, and Reactivity of 1,4,2-Oxa-Tellurazole

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SYNTHESIS, STRUCTURE, AND REACTIVITY OF 1,4,2-OXATELLURAZOLE: A NOVEL TELLURIUM-CONTAINING HETEROCYCLE

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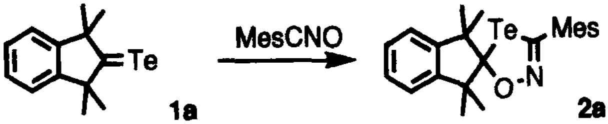
Abstract A novel tellurium containing heterocycle, 1,4,2-oxatellurazole, was characterized by X-ray crystallographic analysis which showed a remarkably small C-Te-C bond angle (79.4°), and its 1,3-dipolar cycloreversion is discussed.

INTRODUCTION

Tellurium containing ring systems are of current interest in heterocyclic chemistry.1) Carbon-chalcogen double bond compounds are known to be useful for the formation of chalcogen containing heterocycles via cycloaddition reactions.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)



1,4,2-OXATELLURAZOLE

As shown in Fig. 1, 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 tellurium (II) five-membered ring systems.4) Although it is well known that organotellurium compounds containing nitrogen and/or oxygen atom(s) show stabilized inter- and intramolecular Te-N/Te-O interactions, a search for interaction contacts in **2a** reveals no significant interaction around the tellurium.

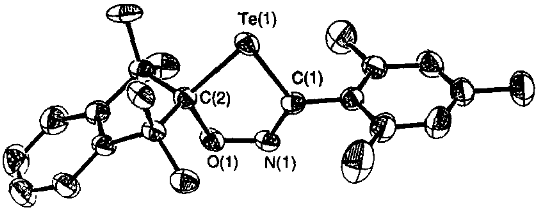
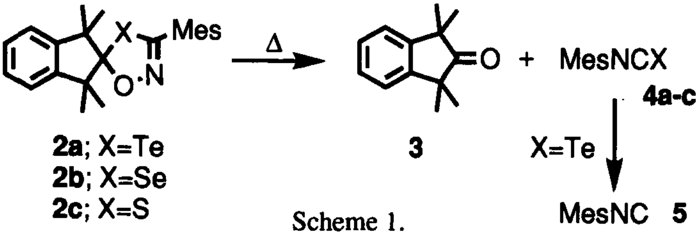


Fig. 1. *ORTEP* drawing of 1,4,2-oxatellurazole **2a** with thermal ellipsoid plot (30% probability).

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 via intermediary isotellurocyanate **4a** (Scheme 1). The thermolysis of oxaselenazole **2b** and oxathiazole **2c** 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.[5]

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