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1,1,3,3-Tetramethylindantellone, the First Telluroketone Stable in Solution

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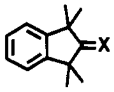
In recent years the chemistry of multiple-bond compounds of heavier typical elements has been a subject of continuing interest.[1] Among these are compounds with a carbon–chalcogen double bond like thio- and selenoketones[2] (or aldehydes[3]), which have been intensively studied and include some stable species. For a telluroketone, however, neither the synthesis of a stable species nor the spectroscopic observation of such has been described,[4] although some scattered examples of stable telluroesters[5a–c] and telluroamides[5d–f] as well as the transition-metal complexes of telluroketones (or aldehydes)[6] have been reported.

We now report the first example of a telluroketone, 1,1,3,3-tetramethylindantellone (**1a**), stable in solution at ambient temperature, which enables the first observation of interesting spectroscopic properties (^{13}C, ^{125}Te NMR, and UV/vis) and novel reactivities (1,3-dipolar cycloaddition and ene reaction) of a genuine telluroketone.



1a: X=Te **1c**: X=S
1b: X=Se **1d**: X=O

We took advantage of the thermal cycloreversion of a novel heterocycle, 1,3,4-telluradiazoline (**2**),[7] for the synthesis of a telluroketone (Scheme I). Although **2** was stable at 80 °C for 6 h in the solid state without any appreciable decomposition, it gradually decomposed in solution even at room temperature. A carefully degassed $CDCl_3$ solution of **2** (ca. 0.02 M) in a sealed tube was subjected to thermolysis in the NMR probe. The thermolysis proceeded best around 80 °C although it was carried out in the temperature range of 60–100 °C. The reaction could similarly be performed in benzene. Monitoring by ^{1}H NMR revealed the completion of the thermolysis for about 4 h and the quantitative formation of telluroketone **1a** and olefins **4** and **5** produced from diazo compound **3**, indicating clean cycloreversion of **2** into **1a** and **3**.[8]

Surprisingly, **1a** is very stable in a dilute solution prepared in the above-mentioned way, surviving after heating at 80 °C for as long as 6 h. However, **1a** is extremely sensitive to oxygen and light, decomposing to give the corresponding ketone **1d** and ditelluride **6**, respectively. The formation of **1a** was confirmed by the following spectral data and chemical reactivities: ^{1}H NMR δ ($CDCl_3$) 1.61 (s, 12 H), 7.30 (s, 4 H); ^{13}C NMR δ ($CDCl_3$) 30.3 (q), 79.4 (s), 124.0 (d), 127.9 (d), 147.2 (s), 301.0 (s); ^{125}Te NMR δ ($CDCl_3$) 2858.3; UV/vis λ_{max} ($CHCl_3$) 825 (ϵ 100) nm.[9]

The tellurocarbonyl carbon resonates at 301 ppm, which is, to our knowledge, the most deshielded carbon ever observed in a neutral molecule.[2e,10] This signal is shifted significantly downfield relative to those for C = X (X = Se, S, O) of the other analogs **1b** (δ 294.0),[11a] **1c** (δ 282.1),[11b] and **1d** (δ 226.0)[11a] and for C = Te of tellurocarbonyl compounds perturbed by the mesomeric effect of α-heteroatoms [e.g., t-Bu(C=Te)OCH$_2$(t-Bu) δ 229.4,[5a,b] t-Bu(C=Te)OSiMe$_3$ δ 251.2[5c]].

The ^{125}Te NMR shift of **1a** (2858 ppm) is also unique, being at much lower field than that of a telluroester [e.g., t-Bu(C=Te)-OSiMe$_3$ δ 1418].[5c] This is the most deshielded ^{125}Te signal so far observed for organotellurium compounds.[12]

The visible spectrum of **1a** ($CHCl_3$, 80 °C) showed λ_{max} 825 nm,[13] which disappeared gradually during several hours even by intermittent irradiation with monitoring light of the spectrometer resulting in the appearance of a new absorption of ditelluride **6** at 400 nm. The absorption at 825 nm, most likely assignable to

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(9) The molar extinction coefficient (ϵ) was obtained by assuming the quantitative formation of **1a** from **2**.

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(13) The color of the solution was green soon after it was taken out of the dark but turned yellow very rapidly even under a fluorescent lamp.

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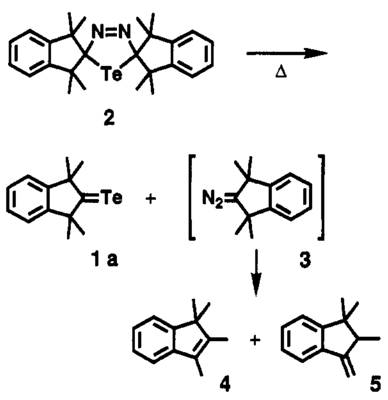
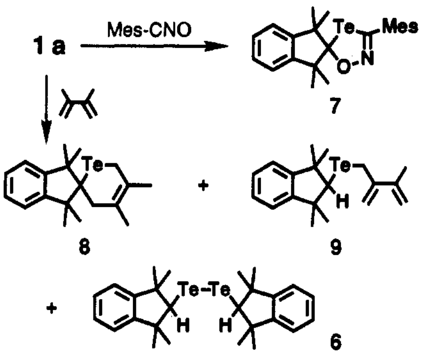
Scheme I



the n–π^* transition of the C=Te bond, is the longest among the carbon—chalcogen double-bond compounds (**1b** 667 nm,[14] **1c** 527 nm[14]).[2]

These spectroscopic observations clearly indicate the monomeric nature of **1a**, which was also supported by its chemical reactivities (Scheme II).[15] Reaction of **1a** with an equimolar amount of mesitonitrile oxide at 80 °C afforded a novel heterocycle (oxatellurazole **7**) regioselectively in a good yield (70%).[16] This represents the first example of 1,3-dipolar cycloaddition of a telluroketone. The Diels–Alder reaction of **1a** with 2,3-dimethyl-1,3-butadiene proceeded under much milder conditions (100 °C, 2 h) than the corresponding selenoketone **1b** (150 °C, 16 h)[17] to give cycloadduct **8** (24%), ene product **9** (34%), and ditelluride **6** (36%). The formation of **9** is the first demonstration of the ene reactivity of a tellurocarbonyl compound.

Scheme II



Further investigation of the physical and chemical properties of **1a** as well as the application of the telluradiazoline methodology to the synthesis of other telluroketones is currently in progress.

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Supplementary Material Available: Physical and spectral data of products **6–9** (1 page). Ordering information is given on any current masthead page.

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(14) Klages, C. P.; Voss, J. *Chem. Ber.* **1980**, *113*, 2255–2277.

(15) All manipulations were performed in the dark with a subdued red lamp.

(16) The regiochemistry of **7** was determined by its mass spectrum, which gave fragmentation of indanone **1d** and MesNCTe. The thermolysis of **7** afforded **1d** and Mes—N≡C, the mechanism of which will be reported elsewhere.

(17) Minoura, M.; Kawashima, T.; Okazaki, R., unpublished results. The products were the corresponding Diels–Alder adduct (57%) and ene product (19%).