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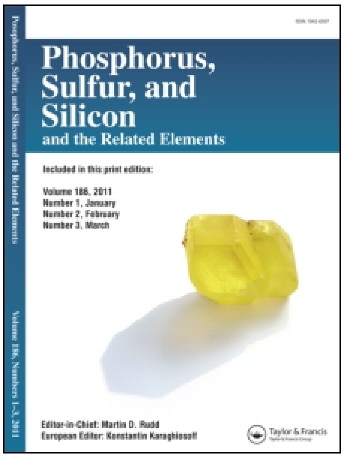

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STABLE TELLUROKETONES: SYNTHESIS AND CHARACTERIZATION

MAO MINOURA,[1] TAKAYUKI KAWASHIMA, NORIHIRO TOKITOH, AND RENJI OKAZAKI*
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Three stable telluroketones were synthesized by taking advantage of the thermal cycloreversion of the corresponding telluradiazolines and exhibited interesting spectroscopic and chemical properties of a genuine carbon-tellurium double bond.

Keywords: telluroketone; tellone; steric protection; double bond

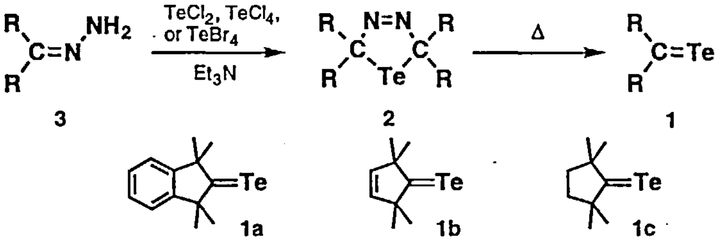
INTRODUCTION

The carbonyl group has been well known as one of the most important functional groups in organic chemistry. In recent years, thioketones[2] and selenoketones[3] have been actively investigated and reliable synthetic methods for stable species have been developed. In contrast, the heaviest chalcogen analogues of carbonyl compounds, tellurocarbonyl compounds, have been much less explored because of their high reactivity which can be ascribed to the unfavorable overlap of C2p–Te5p double bond. However, telluroketones (tellones) without electronic stabilization have proved elusive, although a few telluroketones and telluroaldehydes have been generated as transient species and their existence has been proved *via* cycloaddition.[4]

In this paper, we report the synthesis and characterization of the first stable telluroketones by taking advantage of steric protection.

SYNTHESIS OF TELLUROKETONES

The one-pot reaction of sterically hindered hydrazones **3** with tellurium dichloride or tellurium tetrahalide in the presence of triethylamine in benzene afforded a novel heterocycle, Δ^3-1,3,4-telluradiazoline **2**.[5] The synthesis of telluroketones **1** were achieved by taking advantage of the thermal cycloreversion of **2** (80 °C, in $CHCl_3$) under an inert atmosphere in the dark. The telluroketone **1a** exhibits interesting spectroscopic properties of a genuine carbon-tellurium double bond, i.e., the most downfield chemical shifts (^{13}C, δ 301; ^{125}Te, δ 2858) for a neutral organic molecule and the longest λ_{max} (UV/vis, 825 nm) for a carbon-chalcogen double bond compound.[6] The telluroketones **1b** and **1c**, which were similarly synthesized from **2b** and **2c**, have also similar unique bonding character of a C=Te bond.



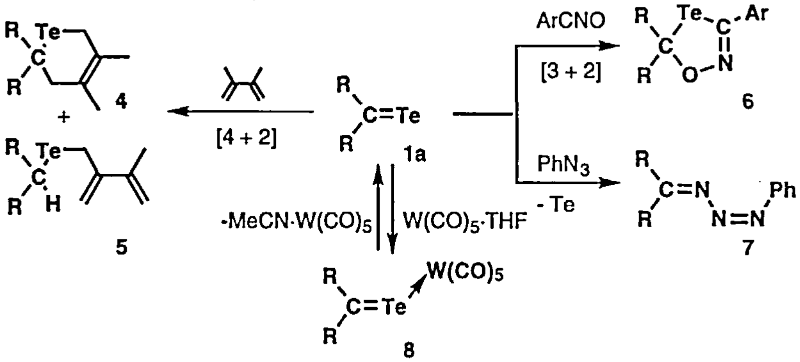
λ_{max} (nm)	825	817	800
$\delta_{C=Te}$	301	301	304
$\delta_{C=Te}$	2858	2789	2694

REACTION OF TELLUROKETONES

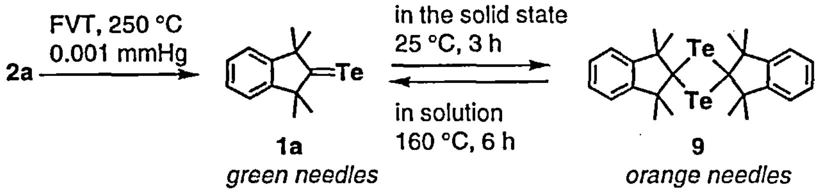
The carbon–tellurium double bond acts of **1a** as a 2π component, in the reaction with 2,3-dimethyl-1,3-butadiene to afford a Diels-Alder adduct **4** along with an ene product **5**. The reaction of **1a** with mesitonitrile oxide resulted in the formation of the corresponding oxatellurazole **6**, as a novel tellurium-containing heterocycle.[7]

Treatment of **1a** with phenyl azide quantitatively afforded triazene **7** which was most likely formed by detelluration from the telluratriazoline obtained via 1,3-dipolar cycloaddition. This is incontrast with the fact that the corresponding thio- and selenoketones reacted with phenyl azide to give the corresponding imine instead of **7**.

The reaction of a stable telluroketone **1a** with $W(CO)_5 \cdot THF$ afforded air stable complex **8**, the X-ray crystal structure of which showed η^1, σ–complexation and *trans* influence of the weakly coordinated telluroketone. The regeneration of a "free" telluroketone was achieved by the ligand exchange reaction of the complex **8** with acetonitrile under mild conditions.[8]



The flash vacuum thermolysis of **2a** at 250 °C under the pressure of 1 x 10^{-3} mmHg led to the isolation of **1a** as green crystals. The NMR and electronic spectra of the green needles were identical with those of the telluroketone obtained from the thermolysis of the telluradiazoline in solution. Interestingly, the green color of the crystalline telluroketone gradually faded away within several hours at room temperature to give orange crystalline 1,3-ditelluretane **9** quantitatively. Dissociation of the ditelluretane **9** into telluroketone **1a** proceeded in $CDCl_3$ solution at 160 °C in a sealed tube over 6 h. Intermittent monitoring by ^1H NMR revealed the quantitative formation of pure **1a**, which was thermally quite stable, surviving after heating at 160 °C for 6 h. In contrast to the reaction in the solid state, any dimerization did not take place in solution.[9]



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[1] Present address: Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 739, Japan

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