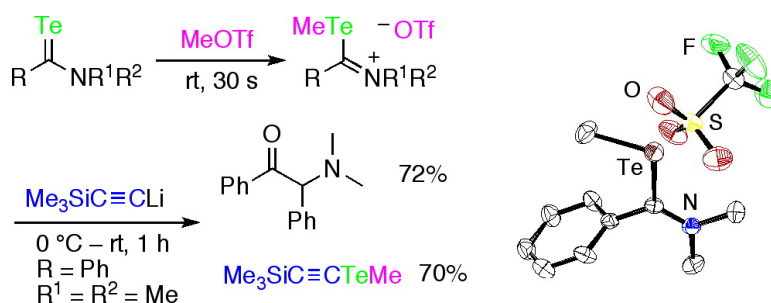


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Acyclic Telluroiminium Salts: Isolation and Characterization

Yuichiro Mutoh,[†] Toshiaki Murai,^{*,†} and Shigeru Yamago[‡]

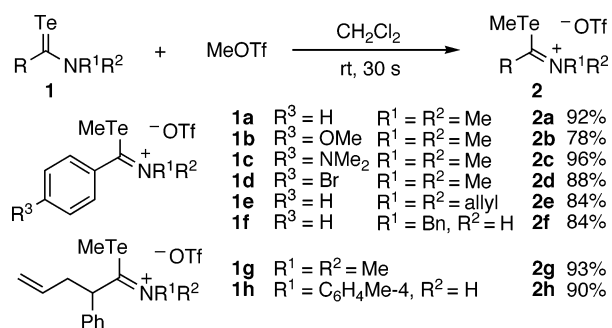
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There is little information available on the chemistry of conjugated ionic species containing tellurium atoms. This may be because of the less efficient delocalization of tellurium lone-pair electrons onto carbon-containing multiple bonds. Spectroscopic and theoretical studies suggested that the interaction of tellurium lone-pair electrons with aromatic rings and alkenyl groups is weaker than that for oxygen and lighter chalcogen atoms.¹ Therefore, tellurium-containing conjugated ionic species would be the least stable among those containing chalcogen atoms because resonance stabilization would not be expected. As anionic species, aliphatic tellurocarboxylic acid salts decompose even under an inert gas atmosphere below $-20\text{ }^{\circ}\text{C}$.² Attention has since been focused on cationic species, for example, hitherto unknown telluroiminium salts in which a tellurenyl group is attached to the carbon atom of an iminium salt.³ During the course of our studies on thio- and selenoamides, we recently isolated various acyclic selenoiminium salts as stable compounds⁴ and also developed a new synthetic method for telluroamides.^{4a} These results inspired us to tackle the synthesis of acyclic telluroiminium salts, and we report here their first successful isolation and characterization.

The methylation of various telluroamides **1** leading to telluroiminium salts **2** was carried out with methyl triflate (Scheme 1). Methylation of tellurobenzamide **1a** was complete within 30 s

Scheme 1



at room temperature to give telluroiminium salt **2a** as a light lemon-yellow solid in 92% yield. A similar methylation gave aromatic telluroiminium salts with methoxy **2b** and dimethylamino **2c** groups and bromine **2d** in their benzene rings in yields of 78–96%. Notably, the highly nucleophilic dimethylamino group was inert toward methyl triflate in the reaction of telluroamide **1c**. Methylation was applied to *N,N*-diallyl telluroamide **1e** and aliphatic telluroamide **1g**, and the corresponding salts **2e** and **2g** were obtained in yields of 84 and 93%, respectively. Secondary telluroamides **1f** and **1h** reacted with methyl triflate to give the salts **2f** and **2h** selectively as (*Z*)-isomers with respect to the C=N double bond in high yields.

The characteristic signals due to the N–H protons of **2f** and **2h** were observed at around 12.5 ppm, which were shifted to lower fields by about 4 ppm compared to the corresponding signals of the starting telluroamides **1f** and **1h**. All of the isolated salts **2** were stable under an argon atmosphere at room temperature, although they decomposed under air, unlike the corresponding selenoiminium salts.

The structural features of the salts **2** in the solid state were elucidated by X-ray molecular structure analysis. An ORTEP drawing of **2a** is shown in Figure 1.⁵ The methyl group of the

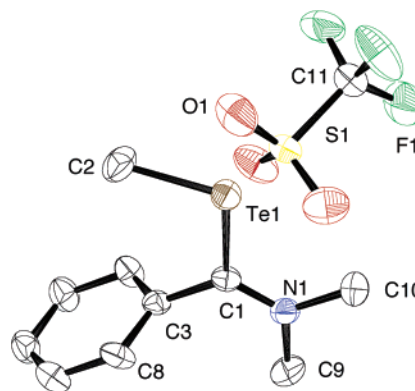


Figure 1. ORTEP drawing of telluroiminium salt **2a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Te1–C1, 2.093(3); Te1–C2, 2.120(4); N1–C1, 1.304(4); N1–C10, 1.472(5); C1–C3, 1.485(5). Selected torsion angles (deg): Te1–C1–N1–C9, 179.7(3); Te1–C1–C3–C8, 89.3(4); N1–C1–Te1–C2, 169.1(3); C3–C1–N1–C9, 2.2(5).

methyltellurenyl (MeTe) group is located cis to the phenyl group with respect to a C–Te bond. There is no apparent intramolecular interaction between the telluroiminium cation and the trifluoromethanesulfonate anion. The torsion angle Te1–C1–N1–C9 in **2a** is $179.7(3)^{\circ}$, and these four atoms are located in the same plane. In contrast, the torsion angle Te1–C1–C3–C8 in **2a** is $89.3(4)^{\circ}$, and the benzene ring is deviated from the plane that is formed by the Te1, C1, and N1 atoms. These results suggest that not the benzene ring but the tellurium p orbital is conjugated with the iminium moiety. This is further supported by the length of the C–Te bond. The length of the Te1–C1 bond in **2a** is 2.093(3) Å, which is longer than the C=Te bond in telluroformamides^{6a} (2.043 and 2.05 Å) and close to that in a tellurourea^{6b} (2.09 Å), but still shorter than the C–Te bond in a telluroimidate^{6c} (2.17 Å).

Spectroscopic properties of selected telluroamides **1** and telluroiminium salts **2** are shown in Table 1, along with those of telluroimidates **3**. In the ¹³C NMR spectra, the signals of the carbon atom of the iminium group of **2** were almost identical to those of the carbon atom of the tellurocarbonyl group of **1**. In the ¹²⁵Te NMR spectra, the signals of the tellurium atom of **2** were shifted upfield by about 112–290 ppm compared to those of the corresponding telluroamides **1**, but were still at a lower field than those

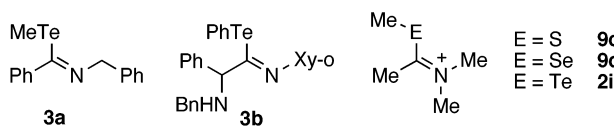
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Table 1. Typical Spectroscopic Data of Selected Telluroamides **1**, Telluroiminium Salts **2**, and Telluroimidates **3**

compound	^{13}C NMR ^{a,b} [ppm]	^{125}Te NMR ^{a,c} [ppm]	$^1J_{\text{C}(\text{sp}^2)\text{-Te}}$ ^d [Hz]
1a	197.1	913.4	557.2
1c	196.8	849.2	545.5
1d	196.4	978.7	559.7
1f	198.3	668.4	567.5
1g	205.7	660.2	572.3
2a	196.5	682.7	464.6
2c	194.7	644.6	446.1
2d	195.4	691.4	467.0
2f	199.2	556.0	473.9
2g	198.3	584.1	483.6
3a^{e,f}	159.8	325.9	342.7
3b^{f,g}	167.3	– ^h	356.4

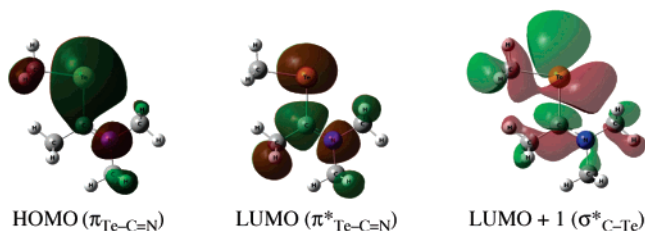
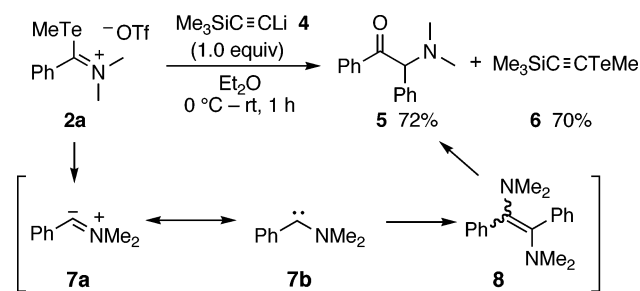
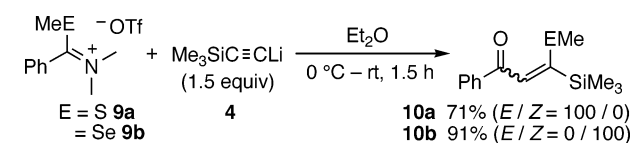
^a CDCl₃ was used as a solvent. ^b The signals of the carbon atom of the tellurocarbonyl or iminium group are shown. ^c The signals were measured at 50 °C. ^d Coupling constants were determined by ^{13}C NMR. ^e Crude product. ^f The structures of **3** are shown in Chart 1. ^g From ref 7. ^h Not observed.

Chart 1

of **3a**. The coupling constants between the carbon and tellurium atoms of **2** (467 ± 18 Hz) were smaller than those of **1** by about 90 Hz, but still greater than those of **3**. These NMR spectra also suggest that the tellurium lone-pair electrons of **2** are delocalized to the C=N double bond, and the C–Te bond of **2** has a partial double-bond character. The significant in-phase contributions from the tellurium and carbon p orbitals to the HOMO ($\pi_{\text{Te-C=N}}$) also characterize the Te–C interaction in the model compound **2i**⁸ (Chart 1, Figure 2).

To examine the reactivity of the isolated salts **2** toward organometallic reagents, aromatic telluroiminium salt **2a** was treated with lithium acetylide **4** in Et₂O (Scheme 2). As a result, two products, that is, α -aminoketone **5** and alkynyl methyl telluride **6**, were obtained in yields of 72 and 70%, respectively. This result is in sharp contrast to the similar reactions of thio- and selenoiminium salts **9**, where single products **10** were obtained (Scheme 3).⁹ This striking difference is attributed to the initial step of the reaction of **2a** and **9** with **4**. In the reaction in Scheme 2, the substitution reaction at the tellurium atom in **2a** with **4** takes place, and the product may be formed via **7** and **8**, whereas in Scheme 3, the addition reaction of **4** to the iminium carbon atom in **9** proceeds.¹⁰

The observed reactivity difference in **2a** is also supported by molecular orbital calculation.⁸ The NPA (natural population analysis)¹¹ charge distribution of **2i** shows a greater positive charge on the tellurium atom (+0.80997) than on the iminium carbon atom (+0.03131). The $\pi_{\text{Te-C=N}}^*$ orbital in **2i** was the main constituent of LUMO, whereas the $\sigma_{\text{C-Te}}^*$ orbital was the main constituent of LUMO + 1 (Figure 2). The LUMO indicates that three out-of-phase orbitals are present around the iminium carbon atom. In contrast, the LUMO + 1 shows the wide backside lobe of the $\sigma_{\text{C-Te}}^*$ orbital. Furthermore, the difference in energy between LUMO + 1 ($\sigma_{\text{C-Te}}^*$) and LUMO ($\pi_{\text{Te-C=N}}^*$) is much smaller than those in sulfur and selenium isologues (**2i**, 0.039 au; **9c**, 0.098 au; **9d**, 0.087 au). On the basis of the orbital phase environment and the small difference in energy, the backside lobe of the $\sigma_{\text{C-Te}}^*$ orbital of **2a** can favorably interact with the $\sigma_{\text{carbanion}}$ orbital.

**Figure 2.** Molecular orbitals of **2i**.**Scheme 2****Scheme 3**

In summary, we have successfully isolated and characterized acyclic telluroiminium salts for the first time. Further studies on the properties and reactivity of conjugate ionic species containing chalcogen atoms are currently in progress.

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Supporting Information Available: Characterization of new compounds **1b–1e** and **1g–2**, crystallographic data for **2a** (PDF, CIF), and NPA charge distributions of **2i**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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