Generation of a Selenoaldehyde, a Selenoketone, and Telluroaldehydes by [3,3] Sigmatropic Rearrangement of Allyl Alkenyl Selenides and Tellurides

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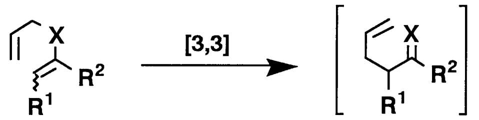
A selenoaldehyde, a selenoketone, and telluroaldehydes were generated by [3,3] sigmatropic rearrangement of allyl alkenyl selenides and tellurides, respectively, and were trapped with 2,3-dimethyl-1,3-butadiene to give the corresponding [4+2] cycloadducts.

Heteroatom-assisted [3,3] sigmatropic rearrangement has been assuming growing importance in the field of organic synthesis, and the reactions have been widely used for the generation of various reactive species containing carbon-chalcogen double bonds. However, in contrast to the extensive studies on Claisen and thio-Claisen rearrangements, thermal reactions of the corresponding selenium and tellurium analogues have been less studied[1,2] in spite of the expectation that such reactions would afford reactive chalcogenocarbonyl compounds such as selenoaldehydes[3-10] and telluroaldehydes.[11,12] In the course of our studies on the generation of highly reactive chalcogenocarbonyl compounds, we have reported a convenient preparation of allyl alkenyl tellurides **2**[13] that would behave as precursors of telluroaldehydes under neutral reaction conditions. Accordingly, our attention has next been directed to the thermal reactions of tellurides **2** and their selenium analogues **1**. In this paper, we wish to describe a novel generation and trapping of a selenoaldehyde, a selenoketone, and telluroaldehydes by the thermal rearrangement of allyl alkenyl selenides **1** and tellurides **2**.



1 (X=Se)
2 (X=Te)

3 (X=Se)
4 (X=Te)

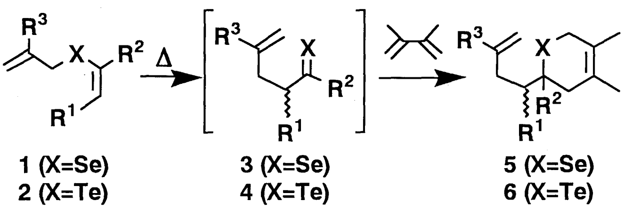
Allyl alkenyl tellurides **2**[13] were prepared by starting from bis(N,N-dimethylcarbamoyl) ditelluride.[14] Allyl alkenyl selenides **1** were also prepared from acetylenes [1) Se/NaBH$_4$/MeOH, 2) terminal acetylenes, 3) NaBH$_4$/MeOH, 4) substituted allyl halides] or from bis(N,N-dimethylcarbamoyl) diselenide[15] through a method similar to that of the tellurium series.[13] In all cases, the physical properties including MS, IR, and ^{1}H NMR spectra were fully consistent with the structures of allyl alkenyl selenides **1** and tellurides **2**. It was noteworthy that both **1** and **2** possessed Z-alkenyl moieties as reported in the addition products of thiols or thiolate anions to acetylenes.[16]

Subsequently, a benzene or Et$_2$O solution of **1** or **2** was heated at 130-140 °C in a sealed tube for several hours under an Ar atmosphere in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene. After the usual workup and the chromatographic purification of the reaction mixture, [4+2] cycloadduct **5** or **6** were isolated in high to modest yields as shown in Table 1. The physical data of the products were fully consistent with the structure of the corresponding [4+2] cycloadducts of selenoaldehyde **3a**, selenoketone **3e**, and telluroaldehydes **4a-c** with the diene.[17] Especially, ^{1}H NMR spectra showed that both **5a**(R^1=CO$_2$Me, R^2=R^3=H) and **5e**(R^1=CO$_2$Me, R^2=Ph, R^3=H) were obtained as an inseparable mixture of two isomers (5:1 and 1:1, respectively), and **6a**(R^1=CO$_2$Me, R^2=R^3=H), **6b**(R^1=CO$_2$Me, R^2=H, R^3=Me), and **6c**(R^1=4-CF$_3$C$_6$H$_4$, R^2=R^3=H) were obtained as sole products. Unstable cycloadduct **6d**(R^1=Ph, R^2=R^3=H) was also detected by ^{1}H NMR measurement of the crude reaction mixture starting from **2d** and diene. The methine protons adjacent to the heteroatoms of **5a**, **6a-d** possessed similar ddd splitting patterns. For example, 2-phenyl-4,5-dimethyl-2,3-dihydro-*2H*-tellurane (**6a**) revealed a signal at δ 4.08ppm as ddd pattern (J=11, 8, 3.9 Hz, respectively). The large J values of the signals suggested the trans-diaxial stereochemistry of the methine protons of **5a** and **6** with the adjacent protons. However, the relative configurations of **5a** and **6** were not characterized from these spectral data.[17,18]

Interestingly, the rearrangement of selenides **1** and tellurides **2** was initiated by heating at about 130 °C in a sealed tube and the [4+2] cycloadducts of telluroaldehydes **4a-c** were obtained in rather lower yields than those of selenoaldehyde **3a** and selenoketone **3e**. This result was due to the higher lability of tellurides **2** and 2,3-dihydro-*2H*-telluranes **6** toward heating, aerobic oxidation, light, and the contact with silica gel or alumina than that of the corresponding selenides **1** and 2,3-dihydro-*2H*-selenanes **5**. It was assumed that, in contrast with selenides **1**, the competitive homolytic C-Te bond cleavage of **2** was unavoidable under such reaction conditions as mentioned above.[19,20] Not only **6d** but also **6a-c** were rather unstable and underwent immediate decomposition with the extrusion of elemental tellurium by standing for a short time at room temperature even under an Ar atmosphere in contrast to the selenium analogues **5**. However, it was also indicated that the introduction of electron-withdrawing group as R^1 substituent was slightly effective for the lowering of the lability of the starting materials **2** and the the products **6**.

Especially, heating of an Et$_2$O solution of allyl alkenyl

Table 1. Generation and Trapping of Selenoaldehyde **3a**, Selenoketone **3e**, and Telluroaldehydes **4a-d** [a]



Substrate				Solvent	Temp	Time	Yield [b]
R^1	R^2	R^3	X		/°C	/h	/%
CO_2Me	H	H	Se	Et_2O	140	6	93 (**5a**) [c]
CO_2Me	Ph	H	Se	Et_2O	140	6	69 (**5e**) [d]
CO_2Me	H	H	Te	Et_2O	130	6	49 (**6a**) [e]
CO_2Me	H	Me	Te	benzene	130	7	30 (**6b**) [e]
$4\text{-}CF_3C_6H_4$	H	H	Te	benzene	130	6	52 (**6c**) [e]
Ph	H	H	Te	benzene	130	6	- (**6d**) [f]
CO_2Me	Ph	H	Te	Et_2O	130	6	- (**6e**) [g]

[a] All reactions were carried out in a sealed tube. [b] Isolated yields. [c] Major:Minor=5:1. [d] Major:Minor=1:1. [e] Major:Minor=1:0. [f] ^1H NMR spectra of the crude reaction product showed that the main product was **6d**. However, isolation of **6d** was unsuccessful owing to the facile decomposition during purification. [g] A complex mixture was obtained.

telluride **2e**(R^2=Ph) in the presence of an excess amount of diene only afforded a rather complicated mixture, and neither the expected telluroketone **4e** nor the corresponding [4+2] cycloadducts **6e** were found in the products of the thermal reaction of **2e**. Segi has reported the trapping of telluroketones with 2,3-dimethyl-1,3-butadiene.[12] In our case, the competitive decomposition of the starting telluride **2e** was thought to occur predominantly. It was assumed that the steric bulkiness of R^2 substituents of the substrates might be a disadvantage in the transition state of [3,3] sigmatropic rearrangement of **2e**.

In conclusion, this work has achieved the novel generation of selenoaldehyde **3a**, selenoketone **3e**, and telluroaldehydes **4a-d** through the [3,3] sigmatropic pathway. Further investigation of the mechanistic insights and the synthetic application of these reactive species are in progress in our laboratory.

References and Notes

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17 Supplementary materials containing the physical data of **5a**, **5e**, **6a**, **6b**, **6c**, and **6d** are available.

18 Selenoaldehydes and telluroaldehydes were assumed to react with 2,3-dimethyl-1,3-butadiene through the favored transition states according to the Cram's rule to form the *anti* isomers.

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20 Heating of a solution of **1** or **2** in the absence of a diene only gave a complex mixture owing to the decomposition of the substrates, and seleno- or tellurocarbonyl compounds were not found in the reaction mixture at all.