Synthesis of 1,2,4-Ditellurazolidines by Oxidative Ring Contraction of 2*H*,6*H*-Tetrahydro-1,5,3,7-ditelluradiazocines

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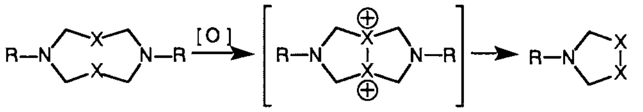
Synthesis of novel five-membered cyclic ditellurides, 4-aryl-1,2,4-ditellurazolidines was achieved by treating 3,7-diaryl-2*H*,6*H*-tetrahydro-1,5,3,7-ditelluradiazocines with oxidizing agents or by aerobic exposure. The oxidative ring contraction of the heterocycles was assumed to proceed through formation and subsequent fragmentation of bicyclic ditellura dications.

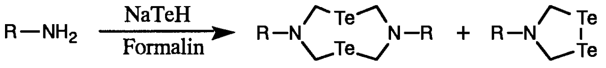
Recently, tellurium-containing heterocycles are of great interest in their synthetic potentiality as the precursors of various heterocycles and the substrates for electroconductive materials. However, the lack of convenient synthetic methods of cyclic polytellurides has impeded the structural and synthetic studies except for some limited cyclic ditellurides.[1] During our studies on cyclic chalcogenoamino acetals, we reported an oxidative ring contraction of 2*H*,6*H*-tetreahydro-1,5,3,7-diselenadiazocines **A** (X=Se) to form 1,2,4-diselenazolidines **C** (X=Se) via dications **B** (X=Se).[2] It was expected that oxidation of tellurium analogues **A** (X=Te) would cause ring contraction to give cyclic ditellurides **C** (X=Te) through a similar process via **B** (X=Te).[3] Along with such expectation, we started the study on 2*H*,6*H*-tetrahydro-1,5,3,7-ditelluradiazocines **A** (X=Te). In this paper, we would like to describe a synthesis and the structural features of **A** (X=Te) as well as the conversion into 1,2,4-ditellurazolidines **C** (X=Te) by treating with an oxidizing agent or by aerobic exposure.



A (X=Se, Te) **B** **C**

Treatment of an aqueous or an ethanolic solution of a primary arylamine (1 mol amount) with formalin (10 mol amounts) and NaTeH (3 mol amounts)[4] at room temperature (R.T.) in an Ar atmosphere according to the reported methods[2,5] afforded 2*H*,6*H*-tetrahydro-1,5,3,7-ditelluradiazocines (**1a**–**e**) as greenish yellow solids. There found no products originated from NaTeH-reduction of formaldimines,[4b,6] and, in all cases, 1,2,4-ditellurazolidines **3** were obtained as main byproducts due to aerobic oxidation of **1** during the usual workup and purification. The ^1H NMR and ^{13}C NMR spectral patterns of **1** measured at 25 °C were quite similar to those of sulfur and selenium analogues **A** (X=S, Se) in all respects.[7] The dynamic ^1H NMR measurement of **1e** (R=*p*-FC_6H_4) in toluene-d_8 at –10 °C exhibited a couple of broad doublet signals assigned to the geminal methylene protons. The signal showed the coalescence point at 10 °C and no significant changing (broad singlet) from 20 °C to 80 °C range. Thus, the $\Delta G^\ddagger$ value for the conformational interconversion of **1e** was estimated as 54.4 kJ/mol. The dynamic conformational feature of **1e** was similar to those of **2a** (X=Se, R=Ph),[2,3,5] and the crown-type conformation was suggested for **1** (X=Te). However, all attempts for X-ray crystallographic analysis of **1a**–**e** were not successful. All the results are shown in Table 1.

Table 1. Preparation of 2*H*,6*H*-Tetrahydro-1,5,3,7-ditelluradiazocines **1**[a]



1 **3**

Amine R	Solvent	Temp / °C	Yield / %[b] 1[c]	3
C_6H_5	H_2O	R.T.	72 (**1a**)	trace (**3a**)
p-$CH_3OC_6H_4$	EtOH/H_2O	R.T.	61 (**1b**)	18 (**3b**)
p-$CH_3C_6H_4$	EtOH/H_2O	R.T.	62 (**1c**)	13 (**3c**)
p-ClC_6H_4	EtOH/H_2O	R.T.	59 (**1d**)	15 (**3d**)
p-FC_6H_4	EtOH/H_2O	-10	41 (**1e**)	11 (**3e**)

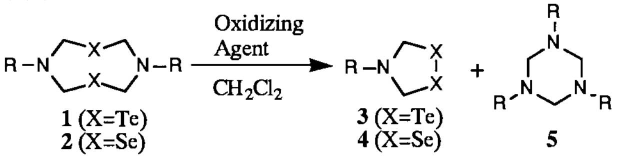
[a]An ethanolic solution of NaTeH[4a] was treated with a primary amine (1 mol amt.) and formalin (10 mol amt.), and the reaction mixture was stirred for 10 min under an Ar atmosphere. [b]Isolated yields. [c]Compounds **1** were gradual oxidized to give **3** during the usual workup and chromatographic purification on silica gel.

Subsequently, a CH_2Cl_2 solution of **1** was treated with air, O_2 gas, or an oxidizing agent (1 mol amount) at –78 °C or at R.T. to give 1,2,4-ditellurazolidines **3** as deep purple crystals in good yields. When the oxidation of **1** was carried out by aerobic exposure, the formation of 1,3,5-triarylhexahydro-1,3,5-triazines **5**[8,9] was accompanied with **3** as main byproducts. The physical data of the products including the MS, IR, ^1H NMR, and ^{13}C NMR spectra, as well as the elemental analysis data, were fully consistent with the structures of **3** and **5**.[8] Especially, the UV–Vis spectra of **3** showed characteristic two absorptions at about 685 and 565 nm regions due to the n–σ* transition of Te–Te bonds,[1f,1j] and the patterns of the UV–Vis spectra were different from those of common dialkyl or diaryl ditellurides. The structural determination of **3** was achieved finally by X-ray crystallographic analysis of **3e** (R=*p*-FC_6H_4), and the ORTEP drawing of **3e** was shown in Figure 1.[10] All the oxidation reactions of **1** are shown in Table 2.

It was assumed that **3** were formed from **1** through oxidative ring contraction via ditellura dications **B** (X=Te) as shown in Scheme 1. The formation of **5** was also explained by the reaction including the formation and trimerization of formaldimines[9] **D** generated from the counterparts of **B** (X=Te).

It is noteworthy that the conversion of **1a** into **3a** by aerobic exposure underwent much faster than that of selenium analogue **2a** into **4a** due to the lower oxidation potential of tellurium atoms of **1** than that of the selenium analogues of **2** and the conformational preference for transannular Te–Te interaction which might accelerate the formation of dication **B** (X=Te)[3e,3f] by oxidation. The calculated intramolecular Te–Te atomic distance of **1a** for the most favored crown-like conformation was estimated to be 3.606 Å from MM2, and the estimated value was much smaller than the sum of the van der Waals radii of tellurium atoms (4.0 Å).[11]

Table 2. Oxidative Ring Contraction of 2*H*,6*H*-Tetrahydro-1,5,3,7-ditelluradiazocines **1**



Substrate	Oxidizing Agent	Temp	Time	Yield /%[a]	
R	(mol amt.)	/ °C	/ h	**3, 4**	**5**
C_6H_5 (**1a**)	air (excess)	R.T.	3	62 (**3a**)[b]	9 (**5a**)
C_6H_5 (**1a**)	O_2 gas (excess)	R.T.	0.5	72 (**3a**)	c
C_6H_5 (**1a**)	NBS (1.1)	-78	0.5	57 (**3a**)	c
C_6H_5 (**1a**)	*m*CPBA (1.1)	-78	0.5	61 (**3a**)	c
p-$CH_3OC_6H_4$ (**1b**)	NBS (1.1)	-78	0.5	62 (**3b**)	c
p-$CH_3C_6H_4$ (**1c**)	NBS (1.1)	-78	0.5	52 (**3c**)	c
p-ClC_6H_4 (**1d**)	NBS (1.1)	-78	0.5	61 (**3d**)	c
p-FC_6H_4 (**1e**)	air (excess)	R.T.	3	64 (**3e**)	12 (**5e**)
C_6H_5 (**2a**)[d]	O_2 gas (excess)	R.T.	128	0 (**4a**)[e]	0

[a]Isolated yields. [b]**1a** was recovered in 27% yield. [c]Not isolated. [d]Reference 2. [e]**2a** was quantitatively recovered.

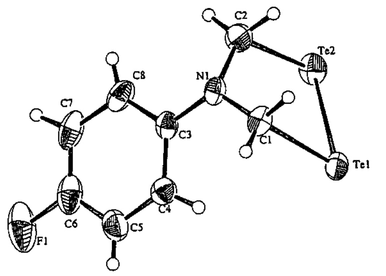
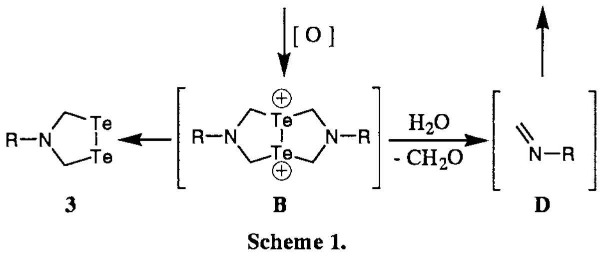


Figure 1. ORTEP Drawing of **3e.** Selected bond lengths (Å) and bond angles (°): Te(1)-Te(2), 2.7561(8); Te(1)-C(1), 2.263(8); Te(2)-C(2), 2.254; C(1)-N(1), 1.404(9); C(2)-N(1), 1.411(10); C(1)-Te(1)-Te(2), 83.8(2); C(2)-Te(2)-Te(1), 85.9(2); Te(1)-C(1)-N(1), 112.2(5); Te(2)-C(2)-N(1), 110.7(5); C(1)-N(1)-C(2), 113.3(7).



Scheme 1.

In conclusion, 1,2,4-ditellurazolidines **3** were synthesized by oxidation of 2*H*,6*H*-tetrahydro-1,5,3,7-ditelluradiazocines **1**. Further attempts for the conversion of **3** into various tellurium-containing heterocycles are in progress in our laboratory.

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References and Notes

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7 Selected NMR spectral data for the methylene signals of **A**. **A** (X=S, R=C_6H_5): ^1H NMR ($CDCl_3$) δ = 5.10 (8H, br.s); ^{13}C NMR ($CDCl_3$) δ = 56.5(t). **A** (**2a**, X=Se, R=C_6H_5): ^1H NMR ($CDCl_3$) δ = 5.10 (8H, br.s); ^{13}C NMR ($CDCl_3$) δ = 51.3 (t). **A** (**1a**, X=Te, R=C_6H_5): ^1H NMR ($CDCl_3$) δ = 5.12 (8H, br.s); ^{13}C NMR ($CDCl_3$) δ = 34.0 (t).

8 Physical data of **1**, **3**, and **5** are available as the supplementary materials.

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10 X-ray crystallographic data for **3e**: Deep green needle, tetragonal, I41/a(#88), a = 18.699(5), c = 11.820(5) Å, V = 4132(2) $Å^3$, Z = 16, D_{calc}= 2.522 g/cm^3, μ(Mo Kα) = 56.10 cm^{-1}, R = 0.027, R_W = 0.027.

11 MM2 calculation of **1a** was carried out by using CS Chem3D Pro Ver. 3.5 on the Macintosh.