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Synthesis and Oxidative Ring Contraction of 1,5,3,7-Dichalcogenadiazocanes. Novel Formation of 1,2,4-Diselenazolidines, 1,2,4-Ditellurazolidines, and 1,2,3,4,5,7-Pentathiazocanes

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1,5,3,7-Dithiadiazocanes, 1,5,3,7-diselenadiazocanes, and 1,5,3,7-ditelluradiazocanes were prepared from a primary amine, formalin, and H_2S, NaSeH, or NaTeH, respectively. Oxidation of 1,5,3,7-diselenadiazocanes and 1,5,3,7-ditelluradiazocanes using NBS efficiently afforded 1,2,4-diselenazolidines or 1,2,4-ditellurazolidines, respectively. In contrast, treatment of 1,5,3,7-dithiadiazocanes with bromine-elemental sulfur or disulfur dichloride (S_2Cl_2) afforded 1,2,3,4,5,7-pentathiazocanes. An unusual oxidative conversion of 1,5,3,7-dichalcogenadiazocanes into these products was assumed to proceed through in situ formation of 1,5,3,7-dichalcogenadiazabicyclo[3.3.0]octane-type dications.

Recently, several heterocycles containing heavy chalcogen atoms are of great interest due to their structures, reactivities, and their synthetic potentiality as novel precursors for various useful heterocycles and new substrates for electroconductive organic materials, and current studies have concentrated on the synthesis and reactions of cyclic polychalcogenides.[1,2] However, in spite of their potential applications, such as antibacterial drugs, natural flavors, and industrial vulcanizing agents, there are only a few reports on macrocyclic polysulfides because they are difficult to prepare and are labile in the presence of various reagents.[3–15] The lack of convenient synthetic methods for cyclic polyselenides and polytellurides has also impeded the structural and synthetic studies of these compounds except for some limited cyclic diselenides and ditellurides.[16–26] During our studies on cyclic chalcogenoacetals, we have reported a variety of chemical conversions of cyclic polychalcogenoacetals and polychalcogenoaminoacetals including 1,3,5-triselenanes,[27,28] 5,6-dihydro-1,3,5-dithiazinanes,[29,30] 6*H*-1,3,5-oxachalcogenazines,[31,32] and 1,5,3,7-dichalcogenadiazocanes **A** (X = S, Se, and Te).[33–35] It was expected that oxidation of conformationally flexible eight-membered aminochalcogenoacetals **A** would undergo transannular chalcogen–chalcogen interaction to give 1,5,3,7-dichalcogenadiazabicyclo[3.3.0]octane-type dications **B**,[36–51] which would undergo further fragmentation to give five-membered cyclic dichalcogenides **C** (X = Se and Te) or the related macrocyclic polysulfides via cyclic disulfides **C** (X = S)[35] by nucleophilic attack on the methylene carbons of **B**.[52–55] In this paper, we describe the oxidative ring contraction of 1,5,3,7-dichalcogenadiazocanes **A** (X = S, Se, and Te) to give 1,2,4-dichalcogenazolidines **C** (X = Se and Te) or the novel cyclic polysulfides, 1,2,3,4,5,7-pentathiazocanes **D** (X = S). An unusual oxidative conversion of **C** (X = Se and Te) into the corresponding perhydro-1,3,5-triazines is also reported in this paper (Scheme 1).

Results and Discussion

Preparation and Conformational Features of 1,5,3,7-Dithiadiazocanes (1), 1,5,3,7-Diselenadiazocanes (2), and 1,5,3,7-Ditelluradiazocanes (3). 3,7-Dialkyl- and 3,7-diaryl-1,5,3,7-dithiadiazocanes **1a–1g** were prepared by the reaction of a primary amine, formalin, and H_2S gas according to the reported methods.[56–59] Compounds **1a–1g** were stable toward air and could be stored for a long time. In the ^{1}H NMR spectra of **1a–1f**, a broad singlet in the signals of 4.10–4.90 ppm regions was observed. Lehn et al. have studied the conformational analysis of 1,5,3,7-dithiadiazocane rings by using variable temperature ^{1}H NMR measurement, and they reported that the conformational interconversion proceeded slowly at room temperature and that the $\Delta G^{\ddagger}$ value for the interconversion between the two preferred conformations, i.e., a crown and a chair-boat conformation, is approximately 13.4–14.8 kcal mol^{-1}.[60] Grandjeans et al. also reported the X-ray crystallographic study on **1f** (R = CH_3), in which it was shown that the 1,5,3,7-dithiadiazocane ring is in a crown-type conformation in the solid state and the atomic distance between the S-1 and S-5 atoms of **1f** is 3.976 Å.[61]

1,5,3,7-Diselenadiazocanes (**2a–2g**) and 1,5,3,7-ditelluradiazocanes (**3a–3e**) were synthesized by modifying Draguet's method,[58] in which an ethanolic solution of a primary amine was treated with formalin and NaSeH[62] or NaTeH,[63,64] respectively. In the synthesis of **3**, no byproducts originating from NaTeH- or H_2Te-induced reduction of formaldimines were found,[65–70] and 1,2,4-ditellurazolidines **6a–6e** were obtained as major byproducts involving tellurium due to further aerobic

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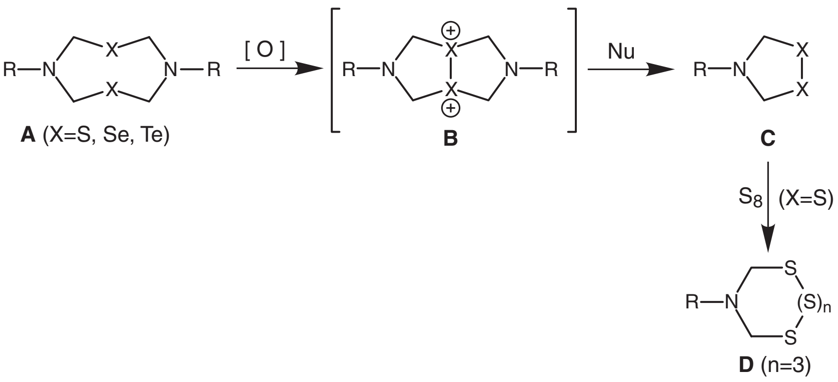


Scheme 1. Oxidative ring contraction of 1,5,3,7-dichalcogenadiazocanes **A** (X = S, Se, and Te).

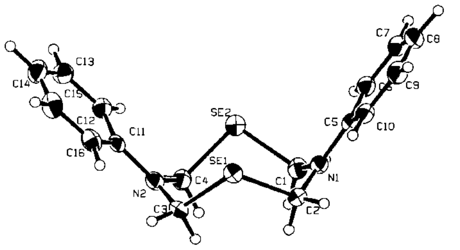


Fig. 1. ORTEP drawing of 1,5,3,7-diselenadiazocane **2a**.

oxidation of **3** during workup and chromatographic purification. All physical data, including MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, were fully consistent with the structures of **2a**–**2g**, and were also identical to the reported data. The structure of **2a** ($R = C_6H_5$) was determined by X-ray crystallographic analysis, and the ORTEP drawing of **2a** is shown in Fig. 1. The crystal data of **2a** indicated that the eight-membered heterocyclic ring of **2** is in a crown-type conformation, in which two selenium atoms were located close to each other and the atomic distance between the two selenium atoms was 3.858 Å. The transannular atomic distance between the Se-1 and Se-5 atoms was thought to be small enough to cause a facile cationic interaction accompanied by minimal motion of the atoms of the substrates **2** during the oxidation step.

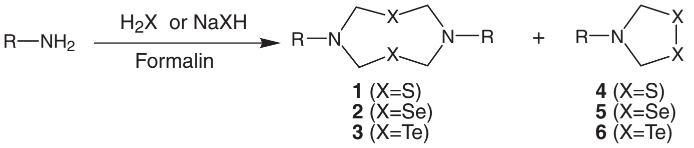
However, attempts for structurally characterize **3a**–**3e** by X-ray crystallography were not successful due to their instability toward air and light. The ^{1}H NMR and ^{13}C NMR spectral patterns of **3**, measured at 25 °C, were similar to those of sulfur and selenium analogues, **1** (X = S) and **2** (X = Se), respectively. In the dynamic ^{1}H NMR spectrum of **3e** ($R = p\text{-}FC_6H_4$) in toluene-d_8 at −10 °C, a couple of broad doublet signals assigned to the *gem*-methylene protons were observed. The signals coalesced at +10 °C, and no significant changes were observed in the range of 20–80 °C. Thus, the approximate $\Delta G^{\ddagger}$ value for the conformational interconversion of **3e** was estimated to be 54.4 kJ mol^{-1} (=13.0 kcal mol^{-1}). The dynamic conformational feature of **3e** was similar to those of **2a** ($R = C_6H_5$),[33,36–51,56–59] and the crown conformation was strongly suggested for the most preferred conformation of **3**. All the results from the syntheses of 1,5,3,7-dichalcogenadiazocanes **2** and **3** are summarized in Table 1.

Oxidative Ring Contraction of 1,5,3,7-Diselenadiazocanes (2) and 1,5,3,7-Ditelluradiazocanes (3). A CH_2Cl_2 solution of NBS (1.1 mol amt.) was added dropwise to a CH_2Cl_2 solution of 1,5,3,7-diselenadiazocane **2a** ($R = C_6H_5$) at −78 °C, and the reaction mixture was stirred for 3 h under an Ar atmosphere. After quenching the reaction with an aqueous NaOH solution, the usual workup, and purification of the crude products by column chromatography on silica gel, 4-phenyl-1,2,4-diselenazolidine (**5a**) was obtained as stable reddish brown prisms in 83% yield along with *N*-(anilinomethyl)succinimide **7a** (85%).[71] Other 1,5,3,7-diselenadiazocanes **2c**, **2f**, and **2g** were also converted into the corresponding 1,2,4-diselenazolidines **5** in high yields by treating with NBS in a similar method as shown above. Treatment of **2** with other oxidizing agents such as *m*CPBA and *t*-BuOOH, as well as the treatment of an CH_3CN solution of **2** with a catalytic amount of $CuCl_2 \cdot 2H_2O$ (0.1 mol amt.) under an aerobic condition, was also effective for the conversion from **2** to **5**. The structures of **5** were confirmed by MS, IR, ^{1}H NMR, ^{13}C NMR spectroscopies, and elemental analysis. The structure of **5c** ($R = p\text{-}CH_3OC_6H_4$) was determined by X-ray crystallographic analysis, and the X-ray data showed a unique 1,2,4-diselenazolidine ring system with a Se–Se bond (2.331 Å) and a quasi-axial *p*-methoxyphenyl substituent on the nitrogen atom. It is worth noting that no intermolecular attractive interaction between the selenium atoms of different molecules of **5** was observed in the crystal lattice. The ORTEP drawing of **5c** is shown in Fig. 2.

In contrast with the selenium series, 1,5,3,7-ditelluradiazocanes **3** underwent facile oxidative ring contraction to give the corresponding 1,2,4-ditellurazolidines (**6**) under rather mild reaction conditions, for example, exposing to air, O_2 gas, or treating with an oxidizing agent (1.0 mol amt.) at −78 °C or at rt, etc., and the formation of perhydro-1,3,5-triazinanes (**8**) was accompanied as major byproducts in each reaction. The physical data of the products including the MS, IR, ^{1}H NMR, and ^{13}C NMR spectra as well as the elemental analysis data were fully consistent with the structures of **6** and **8**. The structure of **6e** ($R = p\text{-}FC_6H_4$) was determined by X-ray crystallographic analysis, and an ORTEP drawing of **6e** is shown in Fig. 3. It is worth noting that **6e** possessed a slightly longer Te–Te bond (2.756 Å) than those of the reported bond lengths of the common acyclic dialkyl ditellurides. The UV–vis spectra of **6** also had two characteristic absorptions at about 685 and 565 nm due to the n–σ^* transition of Te–Te bonds,[21,25] and all of the UV–vis spectral patterns of **6a**–**6e** were also different from those of common dialkyl or diaryl ditellurides.

Actually, when a CH_2Cl_2 solution of 1,2,4-diselenazolidine

Table 1. Preparation of 1,5,3,7-Dichalcogenadiazocanes **1**–**3**



R	X (H_2X)	X (NaXH)	Solvent	Temp /°C	Time /min	Yield/%[a)]	
						1, **2**, **3**	**4**, **5**, **6**
C_6H_5	S	—	C_2H_5OH	rt	1440	82 (**1a**)	0
p-ClC_6H_4	S	—	C_2H_5OH	rt	1440	63 (**1b**)	0
p-$CH_3OC_6H_4$	S	—	C_2H_5OH	rt	1440	81 (**1c**)	0
p-$CH_3C_6H_4$	S	—	C_2H_5OH	rt	1440	79 (**1d**)	0
CH_3[b)]	S	—	H_2O	rt	120	22 (**1f**)	0
c-C_6H_{11}	S	—	C_2H_5OH	rt	1440	52 (**1g**)	0
C_6H_5	—	Se	C_2H_5OH	rt	120	72 (**2a**)	0
p-$CH_3OC_6H_4$	—	Se	C_2H_5OH	rt	120	89 (**2c**)	0
CH_3[b)]	—	Se	C_2H_5OH	rt	120	64 (**2f**)	0
c-C_6H_{11}	—	Se	C_2H_5OH	rt	120	92 (**2g**)	0
C_6H_5	—	Te	H_2O	rt	10	72 (**3a**)[c)]	trace (**6a**)
p-ClC_6H_4	—	Te	C_2H_5OH/H_2O	rt	10	59 (**3b**)[c)]	15 (**6b**)
p-$CH_3OC_6H_4$	—	Te	C_2H_5OH/H_2O	rt	10	61 (**3c**)[c)]	18 (**6c**)
p-$CH_3C_6H_4$	—	Te	C_2H_5OH/H_2O	rt	10	62 (**3d**)[c)]	13 (**6d**)
p-FC_6H_4	—	Te	C_2H_5OH/H_2O	−10	10	41 (**3e**)[c)]	11 (**6e**)

a) Isolated yields based on the starting primary amines. b) $CH_3NH_2 \cdot HCl$ was used in place of CH_3NH_2. c) Compounds **3** were gradually converted into **6** during the usual workup and chromatographic purification on silica gel.

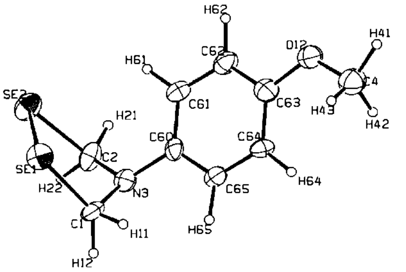


Fig. 2. ORTEP drawing of 1,2,4-diselenazolidine **5c**.

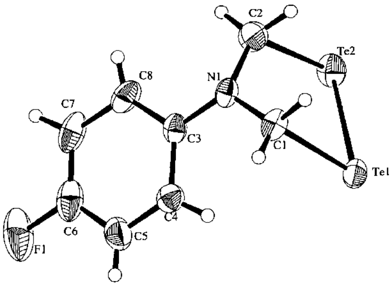


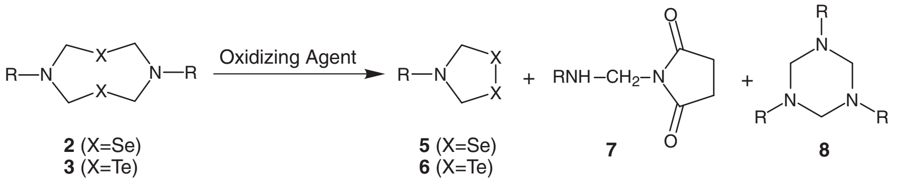
Fig. 3. ORTEP drawing of 1,2,4-ditellurazolidine **6e**.

5c was treated with NBS (1.1 mol amt.) at −78 °C for 1 h under an argon atmosphere, perhydro-1,3,5-triazine **8c** (R = p-$CH_3OC_6H_4$) and succinimide **7c** (R = p-$CH_3OC_6H_4$) were obtained in 63 and 4% yields, respectively, along with the extrusion of elemental selenium, while *m*CPBA oxidation of 1,2,4-ditellurazolidine **6a** (R = C_6H_5) also gave **8a** (R = C_6H_5) in 35% yield.[72,73] These results strongly indicated that compounds **8** were afforded through the oxidation of **6** during the reaction of **3** with oxidizing agents. However, all attempts to trap or to detect directly the precursors of **8**, such as *N*-arylformaldimines, were not successful, and the reaction pathway on the conversion of cyclic dichalcogenides **5** and **6** into perhydro-1,3,5-triazines **8** has not yet been clarified at this time. All the results of oxidative ring contraction of **2** and **3** are shown in Table 2.

Oxidation of 1,5,3,7-Dithiadiazocanes (1) by Using Br_2-Elemental Sulfur or Disulfur Dichloride. A CH_2Cl_2 solution of 1,5,3,7-dithiadiazocanes **1** bearing aromatic substituents at the N-3 and N-5 atoms was treated with Br_2 (1.1 mol amt.) at −78 °C, and in all cases 1,2,3,4,5,7-pentathiazocanes **9** were obtained in moderate yields along with perhydro-1,3,5-thiadiazines **10**[74,75] and insoluble polymeric products **11** in some cases. Yields of **9** were dramatically improved by treating **1** with Br_2–S_8 or S_2Cl_2. However, the optimal amount of S_2Cl_2 for the reactions was just 1.5 mol amt. for **1**, and the use of more than 2.0 molar amount of S_2Cl_2 mainly afforded **11**. In contrast, treatment of **1** bearing alkyl substituents on the N-3 and N-7 positions only gave a complex mixture. All of the results of the conversion of **1** into **9** are summarized in Table 3. The structure of **9a** (R = C_6H_5) was determined by X-ray crystallographic analysis, and an ORTEP drawing is shown in Fig. 4. Compound **9a** possesses an eight-membered cyclic pentasulfide ring system with a crown-type conformation, which is quite similar to those of the reported eight-membered polysulfides,[61,76–86] such as 1,5,3,7-dithiadiazocane **1e**, S_8, S_8O, and heptathiaphosphocanes.

Interestingly, 1,2,4-dithiazolidines **4** were not found at all in the crude products in the cases of the reaction of **1** with Br_2, Br_2–S_8, or S_2Cl_2 in contrast to the selenium and tellurium analogues. Compounds **9** were unexpectedly stable in air at rt and were unreactive toward various oxidizing agents, such as *m*CPBA, aq. H_2O_2 solution, or CH_3CO_3H, even at elevated

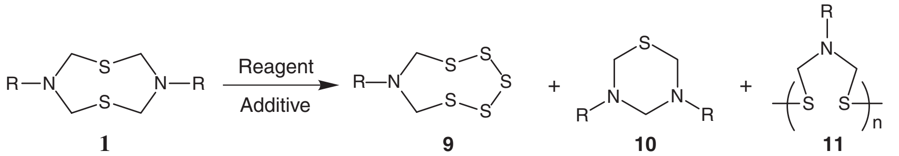
Table 2. Conversion of 1,5,3,7-Dichalcogenadiazocines (**2**, **3**) into 1,2,4-Dichalcogenazolidines (**5**, **6**)



Substrate			Reagent	Solvent	Temp	Time	Yield/%a)		
R	X	**2**, **3**	(mol amt.)		/°C	/h	**5**, **6**	**7**	**8**
C_6H_5	Se	**2a**	NBS (1.1)	CH_2Cl_2	−78	2	83 (**5a**)	85 (**7a**)	0
C_6H_5	Se	**2a**	*m*CPBA (1.1)	CH_2Cl_2	0	1	80 (**5a**)	0	0
C_6H_5	Se	**2a**	*t*-BuOOH (1.1)	CH_2Cl_2	rt	25	68 (**5a**)	0	0
C_6H_5	Se	**2a**	$CuCl_2\cdot 2H_2O$ (0.1)b)	CH_3CN	rt	96	54 (**5a**)	0	0
C_6H_5	Se	**2a**	O_2 gas (excess)	CH_2Cl_2	rt	128	0c)	0	0
p-$CH_3OC_6H_4$	Se	**2c**	NBS (1.1)	CH_2Cl_2	−78	2	89 (**5c**)	0	0
p-$CH_3OC_6H_4$	Se	**2c**	$CuCl_2\cdot 2H_2O$ (0.1)d)	CH_2Cl_2	rt	197	88 (**5c**)	0	0
CH_3	Se	**2f**	NBS (1.1)	CH_2Cl_2	−78	2	76 (**5f**)	0	0
c-C_6H_{11}	Se	**2g**	NBS (1.1)	CH_2Cl_2	−78	2	54 (**5g**)	0	0
C_6H_5	Te	**3a**	Air (excess)	CH_2Cl_2	rt	3	62 (**6a**)e)	0	9 (**8a**)
C_6H_5	Te	**3a**	O_2 gas (excess)	CH_2Cl_2	rt	0.5	72 (**6a**)	0	—f)
C_6H_5	Te	**3a**	NBS (1.1)	CH_2Cl_2	−78	0.5	57 (**6a**)	13 (**7a**)	0
C_6H_5	Te	**3a**	*m*CPBA (1.1)	CH_2Cl_2	−78	0.5	61 (**6a**)	0	—f)
p-ClC_6H_4	Te	**3b**	NBS (1.1)	CH_2Cl_2	−78	0.5	61 (**6b**)	0	—f)
p-$CH_3OC_6H_4$	Te	**3c**	NBS (1.1)	CH_2Cl_2	−78	0.5	62 (**6c**)	0	—f)
p-$CH_3C_6H_4$	Te	**3d**	NBS (1.1)	CH_2Cl_2	−78	0.5	52 (**6d**)	0	—f)
p-FC_6H_4	Te	**3e**	Air (excess)	CH_2Cl_2	rt	3	64 (**6e**)	0	12 (**8e**)

a) Isolated yields. b) The reaction was carried out in CH_3CN under O_2 atmosphere. c) **2a** was quantitatively recovered. d) Aerobic reaction condition. e) **3a** was recovered in 27% yield. f) Not isolated.

Table 3. Oxidation of 1,5,3,7-Dithiadiazocanes **1**



Substrate		Reagent	Additive	Solvent	Temp	Time	Yield/%a)		
R	**1**	(mol amt.)	(mol amt.)		/°C	/min	**9**	**10**	**11**
C_6H_5	**1a**	Br_2 (1.1)	S_8 (0.38)	CH_2Cl_2	−78	60	54 (**9a**)	18 (**10a**)	0
C_6H_5	**1a**	S_2Cl_2 (1.5)	—b)	CH_2Cl_2	−95	300	86 (**9a**)	0	trace
C_6H_5	**1a**	NBS (1.1)	—	CH_2Cl_2	−78	360	complex mixture		
C_6H_5	**1a**	*m*CPBA (1.1)	—	CH_2Cl_2	−78	360	0c)	44 (**10a**)	0
p-ClC_6H_4	**1b**	S_2Cl_2 (1.5)	—b)	CH_2Cl_2	−95	420	50 (**9b**)	17 (**10b**)	0
p-$CH_3OC_6H_4$	**1c**	S_2Cl_2 (1.5)	—d)	CH_2Cl_2	−95	300	31 (**9c**)	0	0
p-$CH_3C_6H_4$	**1d**	Br_2 (1.1)	S_8 (0.38)	CH_2Cl_2	−78	10	30 (**9d**)	0	—e)
p-$CH_3C_6H_4$	**1d**	S_2Cl_2 (1.5)	—b)	CH_2Cl_2	−95	300	66 (**9d**)	26 (**10d**)	0
c-C_6H_{11}	**1g**	S_2Cl_2 (1.0)	—b)	CH_2Cl_2	−95	120	complex mixture		

a) Isolated yields. b) An aqueous solution of $Na_2S\cdot 9H_2O$ (2 mol amt.) and S_8 (2 mol amt.) was used for the workup procedure. c) Compound **1a** was recovered in 16% yield. d) A 10% NaOH solution of S_8 (2 mol amt.) was used for the workup procedure. e) Insoluble polymeric byproduct **11** was mainly obtained.

temperature.[78–80] The lack of reactivity of **9** toward oxidizing agents essentially seemed similar to that of elemental sulfur, and further investigation on the chemical behavior of **9** toward various oxidants is required. In contrast, treatment of **9** with nucleophiles, such as propylamine, NaCN, or PPh_3, or reducing agents, such as $NaBH_4$ or $LiAlH_4$, gave a complex mixture, and treating a CH_2Cl_2 solution of **9** with HCl (gas, excess) or $Et_2O\cdot BF_3$ (1.0 mol amt.) mainly afforded insoluble solids (**11**). Further treatment of **9a** with S_2Cl_2 (1.0 mol amt.) at −78 °C to rt also formed the similar polymeric products **11** and elemental sulfur.

Attempt for Direct Observation of Bicyclic Dichalcogena Dications (B) by Using NMR. When a CD_2Cl_2 solution of 1,5,3,7-dithiadiazocane **1a** was treated with S_2Cl_2 (1.5

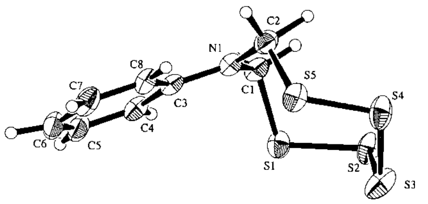
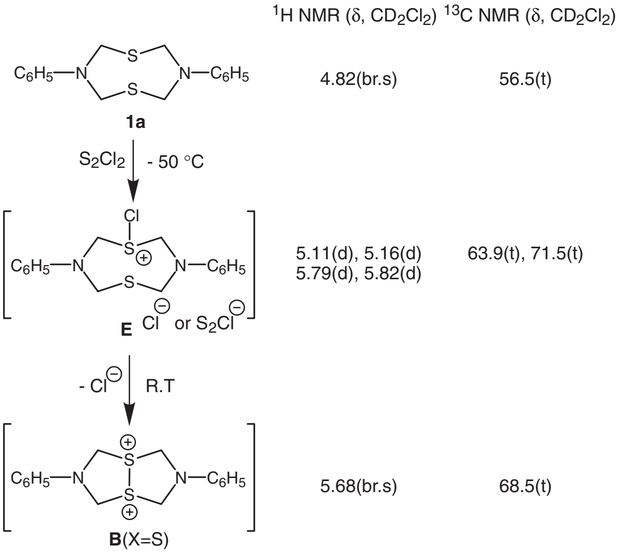


Fig. 4. ORTEP drawing of 1,2,3,4,5,7-pentathiazocane **9a**.

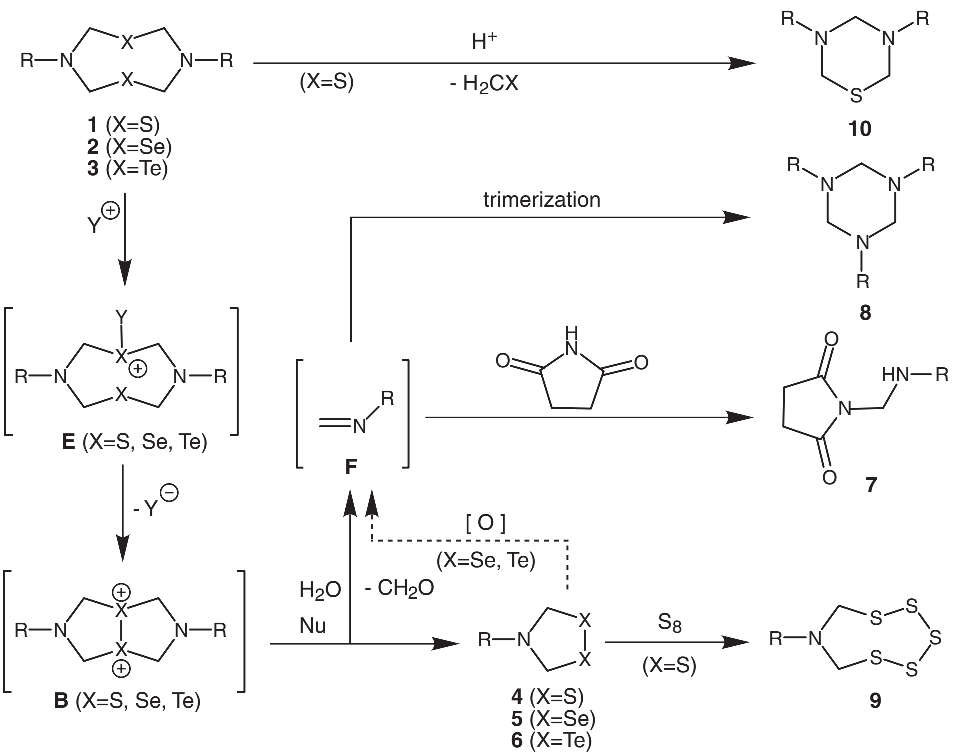


Scheme 2. Change in the chemical shifts of the methylene proton signals and carbons signals through the ^{1}H and ^{13}C NMR monitoring of the reaction of 1,5,3,7-dithiadiazocane **1a** (R = C_6H_5) with S_2Cl_2 in CD_2Cl_2 at −50 °C to rt.

mol amt.) in an NMR tube at −50 °C and the reaction was monitored by using ^{1}H NMR measurement, two pairs of AB-type doublets (5.11 and 5.16 ppm, and 5.79 and 5.82 ppm, respectively) and a broad singlet (5.68 ppm) appeared along with several unidentified signals as soon as S_2Cl_2 was added in the solution along with the disappearance of the original signals of **1a**. Subsequently, the AB-type doublets gradually disappeared along with the raising up of the measuring temperature. In contrast, the singlet signals remained unchanged even when the temperature was raised up to 25 °C. In the ^{13}C NMR spectrum, three triplet signals of the corresponding methylene carbons (63.9, 71.5, and 68.5 ppm) were initially observed and only the 68.5 ppm-signal remained unchanged at higher temperatures. The significant downfield shifts of the methylene signals in the ^{1}H NMR and ^{13}C NMR spectra of the reaction mixture from those of starting **1a** strongly suggested that the unsymmetrical cyclic sulfonium ion **E** formed initially, and the thermally stable secondary species was assumed to be a symmetrical bicyclic dithia dication **B** (X = S). All the results of the ^{1}H NMR and ^{13}C NMR monitoring of the reaction of **1a** with S_2Cl_2 are summarized in Scheme 2. These results suggested that **11** were afforded from **1** through a route involving oxidative transannular S–S bond formation to form **B** (X = S) and the subsequent removal of the half part of **B** by the attack of a nucleophile, such as H_2O, during the usual workup process. Especially, less-strained eight-membered crown-type cyclic polysulfides **9** were mainly afforded as the thermodynamically preferable products through thermal equilibration of the reaction mixture in which intermediary cyclic disulfides **4**, elemental sulfur, and several other cyclic and/or acyclic polysulfides are involved.[77] It is worth noting that the signals of **4a**, **9a**, or **8a** were not observed at all in the NMR spectra, which suggested that these products were formed during the workup procedure.

In contrast, all attempts for the direct detection of the intermediate of oxidation of **2** by NMR monitoring were unsuccessful. When a $CDCl_3$ solution of **2a** was treated with *t*-BuOOH (1.1 mol amt.) in an NMR tube and the reaction mixture was monitored by NMR at 25 °C, no significant signals corresponding to the intermediary dications **B** were observed in the spectrum of the reaction mixture. In our case, the intermediates **B** possess methylene groups adjacent to the cationic selenium atoms. Thus, it was assumed that the fragmentation of **B** was initiated by the attack of nucleophiles on the methylene carbons of **B** to give *N*-(anilinomethyl)succinimide derivatives **7**.[52–55,87] However, an alternative stepwise ring contraction mechanism cannot be excluded.

Plausible Reaction Mechanism for Oxidative Ring Contraction of 1,5,3,7-Diselenadiazocanes (2), 1,5,3,7-Ditelluradiazocanes (3), and 1,5,3,7-Dithiadiazocanes (1). In line with Furukawa's extensive works on the formation of cyclic dichalcogena dications through oxidation of cyclic polychalcogenides,[41–50] diselena dications **B** (X = Se) having a 1,5,3,7-diselenadiazabicyclo[3.3.0]octane skeleton were expected to be generated transiently in the first stage of oxidation of **2**. In our cases, the 1,5,3,7-diselenadiazocane ring in compounds **2** are highly flexible, and the crown-type conformation of the rings, in which the two selenium atoms occupied the closed positions, appears to be the most favorable. 1,5,3,7-Ditelluradiazocanes **3** were more reactive toward oxidizing agents than those of the selenium analogues **2** to form 1,2,4-ditellurazolidines **6** via intermediary ditellura dications **B** (X = Te). It is noteworthy that the conversion of **3** into **6** via exposure to air was much faster than that of selenium analogues **2** which is attributed to the lower oxidation potential of tellurium atom than that of the selenium atom and the conformational preference of **3** for transannular Te–Te interaction induced by oxidation of tellurium atom. On the other hand, the reaction of sulfur analogues **1** with oxidizing agents, such as S_2Cl_2, initially formed unsymmetrical sulfonium ion **E**, and **E** underwent transannular S–S bond formation at higher temperatures to form stable dithia dications **B** (X = S). In other words, halochalcogenonium cation **E** (X = Se and Te) is formed in the primary stage of the reactions and undergoes subsequent facile ring closure to afford bicyclic dication species **B** (X = Se and Te) even at low temperature. Cationic species **B** were assumed to be highly reactive toward nucleophilic agents, even H_2O, and to undergo ring fission to give 1,2,4-dichalcogenazolidines **5** (X = Se) and **6** (X = Te) through the attack of H_2O on the carbon atoms adjacent to the cationic chalcogen atoms in **B**. However, dithia dications **B** (X = S) were efficiently converted into 1,2,3,4,5,7-pentathiazocanes **9** in the presence of elemental sulfur, and 1,2,4-dithiazolidines **4** was not found at all in the reaction mixture. It was suggested that ring strain and repulsive interaction between the lone pairs of the two



Scheme 3. Plausible formation of dichalcogena dications **B** (X = S, Se, and Te) in the conversion of 1,5,3,7-dichalcogenadiazocanes **1**–**3** into 1,2,4-dichalcogenazolidines **5** and **6** or 1,2,3,4,5,7-pentathiazocanes **9**.

neighboring sulfur atoms might reduce the thermal stability of **4** and these factors might be reduced by replacing the sulfur atoms to selenium or tellurium atoms due to the much-larger atomic radii of these heavier chalcogen atoms. Formation of trace amount of perhydro-1,3,5-triazines **8** were also explained by the in situ formation and trimerizaiton of *N*-arylformaldimines $\mathbf{F}^{72,73}$ generated from the counterparts of **B** (X = Se and Te), but an additional or alternative pathway involving the further oxidation of **4** and **5** is also possible.

In addition, small amounts of 5,6-dihydro-1,3,5-dithiazines **10** were formed along with 1,2,3,4,5,7-pentathiazocanes **9** through the reaction of **1** with S_2Cl_2. Our preliminary results on the reactions of **1** with a few Lewis acids indicated that the aminothioacetal moieties of **1** underwent acid-catalyzed cleavage to give **10**. Therefore, it was suggested that the formation of **10** in these cases were also caused by the contamination of trace amount of HCl in S_2Cl_2.

All the plausible pathways of formation of the products through the reactions of **1**–**3** with oxidizing agents are summarized in Scheme 3.

Conclusion

We have found a novel synthesis and unusual oxidative ring contraction of 1,5,3,7-dichalcogenadiazocanes **2** and **3** to afford 1,2,4-dichalcogenazolidines **5** and **6** which are proposed to form via dichalcogena dications **B** (X = Se and Te). As well, 1,5,3,7-dithiadiazocanes **1** were found to convert into 1,2,3,4,5,7-pentathiazocanes **9** through a similar pathway involving the in situ formation of dithia dications **B** (X = S). Further attempts for the conversion of heterocycles **5**, **6**, and **9** into novel heterocyclic ring systems are in progress in our laboratory.

Experimental

Instruments. The melting points were determined with a Büchi 535 micro-melting-point apparatus. ^{1}H NMR spectra were recorded on a Hitachi R-22 (90 MHz) or a Bruker AC-400P (400 MHz) spectrometer, and the chemical shifts of the ^{1}H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Bruker AC-400P spectrometer (100 MHz). ^{77}Se NMR spectra were also recorded on a Bruker AC-400P spectrometer (76 MHz). Mass spectra were recorded on a Hitachi M-2000 mass spectrometer with electron-impact ionization at 20 or 70 eV using a direct inlet system. IR spectra were recorded for thin-film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer. Elemental analyses were performed using a Yanagimoto CHN corder MT-5.

Materials. Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without pretreatment. Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) were dried over P_4O_{10} and were freshly distilled before use. Benzene, hexane, acetonitrile, and triethylamine were dried over calcium hydride (CaH_2) and freshly distilled before use. Diethyl ether and tetrahydrofuran (THF) were dried over lithium aluminum hydride ($LiAlH_4$) and were freshly distilled before use. Ethanol and methanol were dried over anhydrous magnesium sulfate ($MgSO_4$), and were freshly distilled before use. All of the substrates, reagents, and NMR solvents including aniline, *p*-chloroaniline, *p*-methylaniline, *p*-methoxyaniline, *p*-fluoroaniline, cyclohexylamine, methylamine hydrochloride ($CH_3NH_2 \cdot HCl$), propylamine, 37% formalin, iron(II) sulfide (FeS), *N*-bromosuccinimide (NBS), bromine (Br_2), *t*-butyl hydroperoxide, *m*-chloroperbenzoic acid (*m*CPBA), elemental sulfur, elemental selenium, elemental tellurium, disulfur dichloride (S_2Cl_2), boron trifluoride diethyl ether complex ($Et_2O \cdot BF_3$), copper(II) chloride dihydrate

($CuCl_2 \cdot 2H_2O$), sodium metaperiodate ($NaIO_4$), sodium cyanide ($NaCN$), sodium tetrahydroborate ($NaBH_4$), lithium tetrahydroaluminate ($LiAlH_4$), triphenylphosphine, sodium metal, sodium hydroxide, 37% aqueous hydrogen peroxide solution, acetic acid, concentrated hydrochloric acid, deuteriochloroform ($CDCl_3$), dichloromethane-d_2 (CD_2Cl_2), and dimethyl sulfoxide-d_6 (DMSO-d_6) were commercially available reagent grade, and were used without purification.

General Procedure for the Preparation of 1,5,3,7-Dithiadiazocanes (1). H_2S (gas) was treated with 37% formalin (10 mL, 132 mmol) by bubbling, and subsequently the reaction mixture was treated with an ethanol solution (10 mL) of primary amine (30 mmol) at room temperature for 24 h. The reaction was quenched with an excess amount of water, and the reaction mixture was filtered to obtain the insoluble solids. The crude solids were then purified by recrystallization from ethyl acetate to afford 1,5,3,7-dithiadiazocanes **1** as colorless solids.

1a (R = C_6H_5): Colorless plates, mp 179.0–182.0 °C (lit.[52–55] 184.0–185.0 °C); MS (*m/z*) 302 (M^+; 21%), 105 (bp); IR (KBr) 3071, 3028, 3012, 2922, 1596, 1504, 1449, 1368, 1274, 1260, 1217, 1204, 1157, 1004, 869, 753, 744 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.82 (8H, br s), 6.55–7.55 (10H, m); ^{13}C NMR ($CDCl_3$) δ 56.5 (t), 114.8 (d), 119.3 (d), 129.3 (d), 144.0 (s). Calcd for $C_{16}H_{18}N_2S_2$: C, 63.54; H, 6.00; N, 9.26%. Found: C, 63.53; H, 6.04; N, 9.24%.

1b (R = *p*-ClC_6H_4): Colorless plates, mp 175.9–176.6 °C; MS (*m/z*) 370 (M^+; 2%), 45 (bp); IR (KBr) 3043, 1593, 1496, 1449, 1378, 1279, 1209, 1162, 1002, 925, 876, 806, 771, 691, 619 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.81 (8H, br s), 6.78–6.86 (6H, m), 7.21–7.27 (4H, m); ^{13}C NMR ($CDCl_3$) δ 56.9 (t), 115.9 (d), 124.7 (s), 129.2 (d), 142.3 (s). Calcd for $C_{16}H_{16}Cl_2N_2S_2$: C, 51.75; H, 4.34; N, 7.54%. Found: C, 52.06; H, 4.32; N, 7.62%.

1c (R = *p*-$CH_3OC_6H_4$): Colorless plates, mp 142.0–143.0 °C; MS (*m/z*) 362 (M^+; 5%), 135 (bp); IR (KBr) 2935, 1518, 1451, 1397, 1276, 1246, 1206, 1184, 1166, 1038, 1007, 926, 874, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.74 (6H, s), 4.90 (8H, br s), 6.78 (4H, d, $J = 9.0$ Hz), 6.84 (4H, d, $J = 9.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 55.7 (t), 57.4 (q), 114.7 (d), 116.6 (d), 138.4 (s), 153.4 (s). Calcd for $C_{18}H_{22}N_2O_2S_2$: C, 59.64; H, 6.12; N, 7.73%. Found: C, 59.41; H, 6.10; N, 7.70%.

1d (R = *p*-$CH_3C_6H_4$): Colorless plates, mp 155.2–156.8 °C; MS (*m/z*) 330 (M^+; 9%), 46 (bp); IR (KBr) 3003, 2921, 1616, 1520, 1450, 1375, 1267, 1254, 1232, 1200, 1164, 1002, 914, 876, 794, 681, 654 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (6H, s), 4.83 (8H, br s), 6.72 (4H, d, $J = 8.0$ Hz), 7.07 (4H, d, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.5 (q), 57.0 (t), 114.9 (d), 117.9 (d), 129.9 (s), 141.9 (s). Calcd for $C_{18}H_{22}N_2S_2$: C, 65.41; H, 6.71; N, 8.48; S, 19.40%. Found: C, 65.47; H, 6.68; N, 8.44; S, 19.41%.

1f (R = CH_3): Colorless plates, mp 126.0–128.0 °C (lit.[61] 127.0–130.0 °C).

1g (R = *c*-C_6H_{11}): Colorless plates, mp 105.5–107.5 °C; MS (*m/z*) 314 (M^+: 6%), 46 (bp); IR (KBr) 2972, 2927, 2825, 1434, 1378, 1355, 1337, 1330, 1244, 1159, 1131, 1105, 1061, 936, 909, 874, 865, 764, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.22 (6H, m), 1.29–1.37 (4H, m), 1.58–1.60 (2H, m), 1.69–1.74 (4H, m), 1.90–1.93 (4H, m), 2.78–3.02 (2H, m), 4.15 (4H, br s), 4.89 (4H, br s); ^{13}C NMR ($CDCl_3$) δ 24.6 (t), 25.9 (t), 30.4 (t), 54.1 (d), 61.9 (t). Calcd for $C_{16}H_{30}N_2S_2$: C, 61.10; H, 9.61; N, 8.91%. Found: C, 61.07; H, 9.49; N, 8.97%.

General Procedure for the Preparation of 1,5,3,7-Diselenadiazocanes (2). An ethanolic solution (70 mL) of $NaBH_4$ (4.540 g, 120 mmol) was added dropwise to a suspension of elemental selenium powder (4.738 g, 60.0 mmol) in ethanol (30 mL) at 0 °C under an Argon atmosphere, and the reaction mixture was warmed to room temperature. The resulting NaSeH solution was then treated with an ethanolic solution (10 mL) of 37% formalin (10 mL, 32.0 mmol) and subsequently with an ethanolic solution (40 mL) of primary amine (20.0 mmol) for 2 h at room temperature under an Ar atmosphere. The reaction was quenched with an excess amount of water, and the insoluble solids were collected by suction filtration. The solids were washed with dichloromethane and were purified by recrystallization from hexane–chloroform to afford 1,5,3,7-diselenadiazocane **2** as colorless solids.

2a (R = C_6H_5): Colorless needles, mp 184.6–185.8 °C (lit.[60] 185 °C); MS (*m/z*) 105 ($PhNCH_2$; bp), 94 (CH_2Se; 17%, ^{80}Se); IR (KBr) 1595, 1505, 1450, 1375, 1340, 1265, 1235, 1200, 1190, 1150, 1040, 1000, 890, 870, 845, 740, 690, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.10 (8H, br s), 6.70–7.35 (10H, m); ^{13}C NMR ($CDCl_3$) δ 51.3 (t), 115.0 (d), 119.8 (d), 129.6 (d), 143.3 (s). Calcd for $C_{16}H_{18}N_2Se_2$: C, 48.50; H, 4.58; N, 7.07%. Found: C, 48.40; H, 4.51; N, 6.99%.

2c (R = *p*-$CH_3OC_6H_4$): Colorless needles, mp 170.5–171.8 °C; MS (*m/z*) 458 (M^+; 8%, ^{80}Se), 299 (bp), 229 ($M^+/2$; 82%, ^{80}Se); IR (KBr) 2940, 2830, 1500, 1440, 1330, 1040, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (6H, s), 5.06 (8H, br s), 6.71 (4H, br d, $J = 9.1$ Hz), 6.82 (4H, br d, $J = 9.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.5 (t), 55.5 (q), 115.0 (d), 116.6 (d), 137.7 (s), 153.6 (s). Calcd for $C_{18}H_{22}N_2O_2Se_2$: C, 47.39; H, 4.86; N, 6.14%. Found: C, 47.45 H, 4.80; N, 5.98%.

2f (R = CH_3): Colorless needles, mp 157.0–158.0 °C (lit.[60] 160 °C); MS (*m/z*) 274 (M^+; bp, ^{80}Se), 214 ($CH_3N(CH_2Se)_2$; 55%, ^{80}Se), 94 (CH_2Se; ^{80}Se); IR (KBr) 2910, 2870, 1450, 1440, 1400, 1330, 1220, 1160, 1090, 1060, 910, 860, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (6H, s), 4.43 (4H, br s), 4.61 (4H, br s); ^{13}C NMR ($CDCl_3$) δ 39.9 (t), 60.6 (q). Calcd for $C_6H_{14}N_2Se_2$: C, 26.48; H, 5.16; N, 10.30%. Found: C, 26.44; H, 5.16; N, 10.09%.

2g (R = *c*-C_6H_{11}): Colorless needles, mp 140.0–140.3 °C (lit.[60] 140 °C); MS (*m/z*) 410 (M^+; 1%, ^{80}Se), 125 (*c*-$C_6H_{11}N(CH_2)_2$; 42%), 82 (C_6H_{10}; bp); IR (KBr) 2930, 2850, 1440, 1330, 1310, 1280, 1240, 1220, 1130, 1095, 1050, 1020, 850, 760, 650, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.05 (20H, m), 2.74 (2H, tt, $J = 10.0$, 3.7 Hz), 4.27 (4H, br s), 5.01 (4H, br s); ^{13}C NMR ($CDCl_3$) δ 24.5 (t), 25.8 (t), 30.2 (t), 55.7 (d), 57.1 (t). Calcd for $C_{16}H_{30}N_2Se_2$: C, 47.06; H, 7.40; N, 6.86%. Found: C, 46.84; H, 7.54; N, 6.75%.

General Procedure for the Preparation of 1,5,3,7-Ditelluradiazocanes (3). An aqueous solution (20 mL) of $NaBH_4$ (1.248 g, 33.0 mmol) was added dropwise to a suspension of elemental tellurium powder (1.914 g, 15.0 mmol) in water (10 mL) at room temperature under an Ar atmosphere. The resulting aqueous NaTeH solution was then treated with an aqueous solution (10 mL) of 37% formalin (5 mL, 16.0 mmol) and then with an ethanolic solution (10 mL) of a primary amine (5.00 mmol) for 10 min at room temperature under an argon atmosphere. The reaction was quenched with an excess amount of water, and the insoluble solids were collected by suction filtration. The solids were washed with water and then with dichloromethane. The crude solid was washed again with hot benzene to remove the contaminated 1,2,4-ditellrazolidine **6** and was purified by recrystallization from chloroform to afford 1,5,3,7-ditelluradiazocane **3** as yellowish green solids.

3a (R = C_6H_5): Yellowish green crystals, mp 127.0–128.0 °C (dec.); MS (*m/z*) 379 ($M^+ - PhN(CH_2)_2$; 3%, ^{130}Te), 119 (bp); IR(KBr) 3062, 1594, 1502, 1451, 1375, 1372, 1260, 1201, 1166, 993, 800, 751 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.12 (8H, br s), 6.60–

Table 4. Crystal Data for **2a**, **5c**, **6e**, and **9a**

	2a (R = C_6H_5)	**5c** (R = p-$CH_3OC_6H_4$)	**6e** (R = p-FC_6H_4)	**9a** (R = C_6H_5)
Formula	$C_{16}H_{18}N_2Se_2$	$C_9H_{11}NOSe_2$	$C_8H_8FNTe_2$	$C_8H_9NS_5$
Formula weight	396.25	307.11	392.36	279.47
Shape of crystal	Colorless prism	Reddish brown prism	Dark green needle	Colorless prism
Temperature/°C	22	22	22	22
Crystal system	monoclinic	monoclinic	tetragonal	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$I4_1/a$ (No. 88)	$P2_1/c$ (No. 14)
a/Å	13.876(1)	5.787(5)	18.699(5)	13.533(3)
b/Å	5.334(1)	9.993(3)		4.7633(9)
c/Å	21.200(2)	17.828(7)	11.820(5)	19.485(3)
β/°	98.97(1)	94.68(5)		110.15(1)
V/Å^3	1550.0(3)	1027(1)	4132(2)	1179.1(4)
Z value	4	4	16	4
D_{calcd}/g cm^{-3}	1.69	1.985	2.522	1.574
μ(Cu Kα)/cm^{-1}	60.45			87.29
μ(Mo Kα)/cm^{-1}		70.84	56.10	
R	0.032	0.039	0.027	0.065
R_w	0.046	0.056	0.027	0.067

7.25 (10H, m); ^{13}C NMR ($CDCl_3$) δ 34.0 (t), 115.2 (d), 119.8 (d), 130.0 (d), 143.1 (s). Calcd for $C_{16}H_{18}N_2Te_2$: C, 38.94; H, 3.68; N, 5.68%. Found: C, 39.31; H, 3.79; N, 5.53%.

3b (R = p-ClC$_6$H$_4$): Yellowish green crystals, mp 141.0–141.6 °C (dec.); MS (m/z) 531 (M$^+$; ^{35}Cl; 0.1%, ^{130}Te, ^{35}Cl), 413 (M$^+$ − ArN(CH$_2$)$_2$; 2%, ^{130}Te, ^{35}Cl), 153 (ArN(CH$_2$)$_2$; bp, ^{35}Cl); IR (KBr) 3064, 3040, 2999, 2943, 1594, 1496, 1453, 1375, 1320, 1254, 1196, 1164, 1133, 1121, 1086, 989, 807, 792 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.05 (8H, br s), 6.53 (4H, d, $J = 9.0$ Hz), 7.19 (4H, d, $J = 9.0$ Hz). Calcd for $C_{16}H_{16}Cl_2N_2Te_2$: C, 34.17; H, 2.87; N, 4.98%. Found: C, 34.53; H, 2.89; N, 5.06%.

3c (R = p-CH$_3$OC$_6$H$_4$): Yellowish green crystals, mp 110.0–111.0 °C (dec.); MS (m/z) 409 (M$^+$ − ArN(CH$_2$)$_2$; 12%, ^{130}Te), 149 (ArN(CH$_2$)$_2$; bp); IR (KBr) 2991, 2945, 2827, 1580, 1509, 1460, 1374, 1336, 1226, 1207, 1176, 993 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.71 (6H, s), 5.11 (8H, br s), 6.57 (4H, d, $J = 9.1$ Hz), 6.80 (4H, d, $J = 9.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 35.7 (t), 55.6 (q), 115.5 (d), 116.4 (d), 137.4 (s), 153.5 (s). Calcd for $C_{18}H_{22}N_2O_2Te_2$: C, 39.05; H, 4.01; N, 5.06%. Found: C, 38.73; H, 3.89; N, 5.23%.

3d (R = p-CH$_3$C$_6$H$_4$): Yellowish green crystals, mp 117.0–118.0 °C (dec.); MS (m/z) 526 (M$^+$; 0.1%, ^{130}Te), 91 (p-CH$_3$-C$_6$H$_4$; bp); IR (KBr) 2919, 1617, 1518, 1372, 1162, 1127, 993, 802 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.10 (6H, s), 5.28 (8H, br s), 6.53 (4H, d, $J = 9.1$ Hz), 7.00 (4H, d, $J = 9.1$ Hz). Calcd for $C_{18}H_{22}N_2Te_2$: C, 41.45; H, 4.25; N, 5.37%. Found: C, 41.58; H, 4.26; N, 5.04%.

3e (R = p-FC$_6$H$_4$): Yellowish green needles, mp 132.0–132.3 °C (dec.); MS (m/z) 534 (M$^+$; 0.1%, ^{130}Te), 397 (M$^+$ − ArN(CH$_2$)$_2$; 1.5%, ^{130}Te), 109 (FC$_6$H$_4$; bp); IR (KBr) 3051, 1595, 1509, 1457, 1374, 1255, 1234, 1201, 1172, 993, 812 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 5.28 (4H, br s), 5.50 (4H, br s), 6.73 (4H, dd, $J = 9.2$, 4.4 Hz), 7.11 (4H, t, $J = 8.8$ Hz); ^{13}C NMR (DMSO-d_6) δ 33.2 (t), 115.9 (dd, $J_{C–F} = 22.0$ Hz, $J_{C–H} = 18.0$ Hz), 116.5 (dd, $J_{C–F} = 7.3$ Hz, $J_{C–H} = 3.0$ Hz), 140.4 (s), 155.9 (d, $J_{C–F} = 235.4$ Hz). Calcd for $C_{16}H_{16}F_2N_2Te_2$: C, 36.29; H, 3.05; N, 5.29%. Found: C, 36.29; H, 3.36; N, 5.29%.

X-ray Crystallographic Analysis of 2a. A colorless prism of $C_{16}H_{18}N_2Se_2$ having approximate dimensions of 0.25 × 0.30 × 0.30 mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku automated four-cycle diffractometer (AFC5R), equipped with a rotating anode (45 kV, 200 mA), using graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal data are as follows: $a = 13.876(1)$ Å, $b = 5.334(1)$ Å, $c = 21.200(2)$ Å, $\beta = 98.97(1)$°, $V = 1550.0(3)$ Å^3, the space group $P2_1/c$ (No. 14), $Z = 4$, $D_{calcd} = 1.69$ g cm^{-3}, μ(Cu Kα) = 60.45 cm^{-1}. The ω-2θ scan mode with a scan rate of 8° min^{-1} (ω) was employed with a scan range of $1.40 + 0.30 \tan\theta$. A total of unique 2762 reflections within $2\theta = 126$° were collected. The structure was solved by a direct method and refined by a full-matrix least-square method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms found in the successive D-Fourier map were refined with the riding mode. The final cycle of refinement was carried out using 2317 observed reflections within $I_o > 3\sigma(I_o)$ and 200 variable parameters converged to the final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ value of 0.032 and $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w F_o{}^2]^{1/2}$ of 0.046 (Tables 4 and 5).

A Typical Procedure for Oxidation of 1,5,3,7-Diselenadiazocanes (2). A dichloromethane solution (40 mL) of NBS (196 mg, 1.10 mmol) was added dropwise to a dichloromethane solution (150 mL) of 1,5,3,7-diselenadiazocane **2** (1.00 mmol) at −78 °C under a nitrogen atmosphere, and the reaction mixture was stirred at −78 °C for 2 h. The reaction was quenched with an excess amount of 10% aqueous NaOH solution and was extracted with dichloromethane. The organic layer was washed with water and was dried over anhydrous Na$_2$SO$_4$ powder. After removing the solvent in vacuo, the residual crude mixture, containing 1,2,4-diselenazolidine **5** and succinimide **7**, was subjected to chromatographic purification using silica gel. Recrystallization from dichloromethane–hexane gave **5** as dark red solids.

Oxidation of 1,5,3,7-Diselenadiazocane 2a Using Oxygen Gas in the Presence of a Catalytic Amount of Copper(II) Chloride. An acetonitrile solution (110 mL) of 1,5,3,7-diselenadiazocane **2a** (317 mg, 0.80 mmol) was treated with CuCl$_2$•2H$_2$O (14 mg, 0.08 mmol), and an excess amount of oxygen gas was introduced slowly with bubbling to the stirred reaction mixture at room temperature for 4 days. The reaction was quenched with an excess amount of water, and the reaction mixture was subjected to the usual workup. After removing the solvent in vacuo, the residual crude mixture was subjected to chromatographic purification using silica gel. Recrystallization from dichloromethane–hexane gave **5a** in 54% yield as reddish brown needles.

Oxidation of 1,5,3,7-Diselenadiazocane 2c Using Air in the

Table 5. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **2a**

Bond lengths/Å		Bond angles/deg		Torsion angles/deg[a)]	
Se(1)–C(2)	2.002(4)	C(2)–Se(1)–C(3)	98.7(2)	Se(1)–C(2)–N(1)–C(1)	−85.5(3)
Se(1)–C(3)	2.009(4)	C(1)–Se(2)–C(4)	96.7(1)	Se(1)–C(2)–N(1)–C(5)	77.7(3)
Se(2)–C(1)	1.986(4)	C(1)–N(1)–C(2)	116.8(3)	Se(1)–C(3)–N(2)–C(4)	84.9(3)
Se(2)–C(4)	1.986(4)	C(1)–N(1)–C(5)	120.5(3)	Se(1)–C(3)–N(2)–C(11)	−74.9(3)
N(1)–C(1)	1.425(4)	C(2)–N(1)–C(5)	120.4(3)	Se(2)–C(1)–N(1)–C(2)	87.3(3)
N(1)–C(2)	1.410(4)	C(3)–N(2)–C(4)	117.0(3)	Se(2)–C(1)–N(1)–C(5)	75.8(3)
N(1)–C(5)	1.403(4)	C(3)–N(2)–C(11)	120.4(3)	Se(2)–C(4)–N(2)–C(3)	−86.7(3)
N(2)–C(3)	1.420(4)	C(4)–N(2)–C(11)	119.4(3)	N(1)–C(1)–Se(2)–C(4)	−100.4(3)
N(2)–C(4)	1.428(4)	Se(2)–C(1)–N(1)	116.2(2)	N(1)–C(2)–Se(1)–C(3)	95.5(3)
N(2)–C(11)	1.402(4)	Se(1)–C(2)–N(1)	118.4(2)	N(1)–C(5)–C(6)–C(7)	−176.8(3)
		Se(1)–C(3)–N(2)	118.2(2)	N(1)–C(5)–C(10)–C(9)	176.3(3)
		Se(2)–C(4)–N(2)	116.5(2)	N(2)–C(3)–Se(1)–C(2)	−95.2(3)
		N(1)–C(5)–C(6)	120.7(3)	N(2)–C(4)–Se(2)–C(1)	100.0(3)
		N(1)–C(5)–C(10)	121.8(3)	C(1)–N(1)–C(5)–C(6)	170.7(3)
		N(2)–C(11)–C(12)	120.7(3)	C(2)–N(1)–C(5)–C(6)	−171.9(3)
		N(2)–C(11)–C(16)	122.1(3)	C(2)–N(1)–C(5)–C(10)	8.2(4)
				C(3)–N(2)–C(11)–C(12)	165.1(3)
				C(3)–N(2)–C(11)–C(16)	−16.5(4)
				C(4)–N(2)–C(11)–C(12)	−175.8(3)

a) The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Presence of a Catalytic Amount of Copper(II) Chloride. An acetonitrile solution (90 mL) of 1,5,3,7-diselenadiazocane **2c** (319 mg, 0.80 mmol) was treated with $CuCl_2{\cdot}2H_2O$ (12 mg, 0.07 mmol), and the reaction mixture was stirred in air at room temperature for 8 days. The reaction was quenched with an excess amount of water, and the reaction mixture was subjected to the usual workup. After removing the solvent in vacuo, the residual crude mixture was subjected to chromatographic purification using silica gel. Recrystallization from dichloromethane–hexane gave pure 1,2,5-diselenazolidine **5c** in 88% yield as reddish brown needles.

5a (R = C_6H_5): Reddish brown prisms, mp 119.0–120.0 °C (dec.); MS (*m/z*) 279 (M^+; 97%, ^{80}Se), 275 (M^+; bp, ^{78}Se); IR (KBr) 1580, 1485, 1350, 1170, 990, 600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.02 (4H, s), 7.09–7.34 (5H, m). ^{13}C NMR ($CDCl_3$) δ 57.4 (t), 118.8 (d), 124.7 (d), 129.2 (d), 144.8 (s). Calcd for $C_8H_9NSe_2$: C, 34.68; H, 3.27; N, 5.06%. Found: C, 34.77; H, 3.29; N, 4.81%.

5c (R = p-$CH_3OC_6H_4$): Reddish brown needles, mp 111.0–112.0 °C (dec.); MS (*m/z*) 309 (M^+; 39%, ^{80}Se), 147 ($M^+ - Se_2$; 94%), 134 ($M^+ - Se_2 - CH_2 - 1$; bp); IR (KBr) 3042, 2998, 2965, 2839, 1500, 1440, 1350, 1295, 1245, 1030, 970, 830, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.75 (3H, s), 4.97 (4H, s), 6.82 (2H, d, $J = 8.0$ Hz), 7.17 (2H, d, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 55.9 (q), 59.6 (t), 114.9 (d), 121.2 (d), 139.0 (s), 157.6 (s). Calcd for $C_9H_{11}NOSe_2$: C, 35.21; H, 3.61; N, 4.56%. Found: C, 35.42; H, 3.62; N, 4.61%.

5f (R = CH_3): Reddish brown needles, mp 81.0–82.0 °C; MS (*m/z*) 217 (M^+; 66%, ^{80}Se), 57 ($M^+ - Se_2$; bp); IR (KBr) 3010, 2960, 1457, 1438, 1407, 1355, 1308, 1178, 1118, 1077, 1051, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.14 (3H, s), 4.66 (4H, s); ^{13}C NMR ($CDCl_3$) δ 41.2 (t), 64.6 (q). Calcd for $C_3H_7NSe_2$: C, 16.76; H, 3.28; N, 6.51%. Found: C, 16.71; H, 3.27; N, 6.51%.

5g (R = c-C_6H_{11}): Reddish brown needles, mp 68 °C (dec.); MS (*m/z*) 289 (M^+; 6%, ^{80}Se), 124 ($M^+ - Se_2 - 1$; bp); IR (KBr) 3042, 2931, 2851, 1439, 1182, 1063, 920, 819 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10–2.10 (11H, m), 4.80 (4H, s); ^{13}C NMR ($CDCl_3$) δ 24.6 (t), 25.4 (t), 30.4 (t), 56.7 (d), 59.2 (t). Calcd for $C_8H_{15}NSe_2$: C, 33.94; H, 5.34; N, 4.95%. Found: C, 33.30; H, 5.32; N, 4.78%.

7a (R = C_6H_5): Colorless plates, mp 170.0–171.0 °C (lit.[68–70] 171–172 °C); MS (*m/z*) 204 (M^+; 30%); IR (KBr) 3368, 1694, 1604, 1533, 1415, 1184, 1129, 1071, 938, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.65 (4H, s), 4.80 (1H, br s), 4.99 (2H, d, $J = 7.9$ Hz), 6.78–6.80 (3H, m), 7.17–7.21 (2H, m). Calcd for $C_{11}H_{12}N_2O$: C, 64.69; H, 5.92; N, 13.72%. Found: C, 64.44; H, 5.89; N, 13.73%.

General Procedure for Oxidation of 1,2,4-Diselenazolidines (5) or 1,2,4-Ditellurazolidine 6a (R = C_6H_5) Using NBS. A dichloromethane solution (30 mL) of *N*-bromosuccinimide (0.196 g, 1.10 mmol) was added dropwise to a dichloromethane solution (100 mL) of 1,2,4-dichalcogenazolidine **5** or **6** (1.00 mmol) at −78 °C under an argon atmosphere, and the reaction mixture was stirred at −78 °C for 1 h. The reaction was quenched with an excess amount of 10% aqueous NaOH solution, and was extracted with dichloromethane. The organic layer was washed with water and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude mixture, containing succinimide **7** and perhydro-1,3,5-triazine **8**, was subjected to chromatographic purification using silica gel. Recrystallization from ethanol gave **8** as colorless solids.

8a (R = C_6H_5): Colorless needles, mp 140.0–140.5 °C (lit.[72,73] 140.0–141.0 °C); MS (*m/z*) 315 (M^+; 2%), 210 ($M^+ - C_6H_5NCH_2$; 20%), 118 ($C_6H_5N(CH_2)_2$; 12%); IR (KBr) 2942, 2847, 1598, 1499, 1442, 1334, 1163, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.89 (6H, s), 6.84–7.23 (15H, m).

8e (R = p-FC_6H_4): Colorless needles, mp 154.0–155.0 °C; MS (*m/z*) 370 (M^+; 5%), 246 ($M^+ - ArNCH_2$; 50%), 138 ($ArN(CH_2)_2$; 12%); IR (KBr) 2951, 1479, 1450, 1242, 1222, 1200, 1161, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.76 (6H, s), 6.90 (6H, t, $J = 9.0$ Hz), 6.97 (6H, dd, $J = 9.1, 4.6$ Hz). Calcd for $C_{21}H_{18}F_3N_3$: C, 68.28; H, 4.91; N, 11.38%. Found: C, 68.21; H, 4.97; N, 11.33%.

A Typical Procedure for Oxidation of 1,5,3,7-Ditelluradiazocanes (3). A dichloromethane solution (50 mL) of NBS

(98 mg, 0.55 mmol) was added dropwise to a dichloromethane solution (100 mL) of 1,5,3,7-ditelluradiazocane **3** (0.50 mmol) at −78 °C under an argon atmosphere, and the reaction mixture was stirred at −78 °C for 30 min. The reaction was quenched with an excess amount of 10% aqueous NaOH solution, and was extracted with dichloromethane. The organic layer was washed with water and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude mixture, containing 1,2,4-ditellurazolidine **6** and succinimide **7**, was subjected to recrystallization from dichloromethane–hexane gave pure 1,2,4-ditellurazolidine **6** as brownish green solids. The filtrate was subjected to chromatographic purification using silica gel and the subsequent recrystallization from hexane–dichloromethane to afford succinimide **7**.

General Procedure for Aerobic Oxidation of 1,5,3,7-Ditelluradiazocanes (3). A dichloromethane solution (150 mL) of 1,5,3,7-ditelluradiazocane **3** (0.80 mmol) was stirred in air at room temperature for 3 h. The reaction was then filtrated to remove the precipitated elemental tellurium. After removing the solvent of the filtrate in vacuo, the residual crude mixture was subjected to recrystallization to give 1,2,4-ditellurazolidine **6** as brownish green solids.

6a (R = C_6H_5): Brownish green crystals, mp 104.0–104.5 °C (dec.); MS (*m*/*z*) 379 (M^+; 9%, ^{130}Te), 119 ($M^+ - Te_2$; bp); IR (KBr) 3045, 2962, 1597, 1498, 1371, 1249, 1132, 1002, 753, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.37 (4H, br s), 6.90–7.50 (5H, m); ^{13}C NMR ($CDCl_3$) δ 36.6 (t), 118.1 (d), 125.0 (d), 129.3 (d), 144.9 (s). Calcd for $C_8H_9NTe_2$: C, 25.67; H, 2.40; N, 3.74%. Found: C, 25.17; H, 2.40; N, 3.51%.

6b (R = *p*-ClC_6H_4): Metallic green powder, mp 134.0–135.0 °C (dec.); MS (*m*/*z*) 412 (M^+; 4%, ^{130}Te, ^{35}Cl), 153 ($M^+ - Te_2$; bp); IR (KBr) 3088, 3069, 3054, 2972, 1589, 1493, 1457, 1440, 1360, 1312, 1243, 1165, 1131, 1092, 991, 863, 817, 791, 769 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (4H, br s), 7.11 (2H, d, $J = 8.9$ Hz), 7.27 (2H, d, $J = 8.9$ Hz). Calcd for $C_8H_8ClNTe_2$: C, 23.50; H, 1.97; N, 3.43%. Found: C, 23.35; H, 1.82; N, 3.06%.

6c (R = *p*-$CH_3OC_6H_4$): Metallic green plates, mp 111.0–111.5 °C (dec.); MS (*m*/*z*) 409 (M^+; 0.9%, ^{130}Te), 149 ($M^+ - Te_2$; bp); IR (KBr) 3044, 2952, 2932, 1611, 1510, 1470, 1392, 1247, 1182, 1127, 1036, 821 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.76 (3H, s), 5.32 (4H, br s), 6.84 (2H, d, $J = 9.1$ Hz), 7.12 (2H, d, $J = 9.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 38.5 (t), 55.4 (q), 114.5 (d), 119.7 (d), 137.4 (s), 157.3 (s). Calcd for $C_9H_{11}NOTe_2$: C, 26.73; H, 2.74; N, 3.46%. Found: C, 26.66; H, 2.74; N, 3.58%.

6d (R = *p*-$CH_3C_6H_4$): Metallic green needles, mp 111.0–112.0 °C (dec.); MS (*m*/*z*) 393 (M^+; 2%, ^{130}Te), 133 ($M^+ - Te_2$; bp); IR (KBr) 2920, 1516, 1364, 1237, 1166, 1127, 991, 799 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.29 (3H, s), 5.34 (4H, br s), 7.05–7.12 (4H, m); ^{13}C NMR ($CDCl_3$) δ 20.8 (q), 37.4 (t), 117.9 (d), 129.9 (d), 134.8 (s), 141.4 (s). Calcd for $C_9H_{11}NTe_2$: C, 27.83; H, 2.85; N, 3.61%. Found: C, 27.35; H, 2.68; N, 3.43%.

6e (R = *p*-FC_6H_4): Metallic dark green plates, mp 143.0–144.0 °C (dec.); MS (*m*/*z*) 397 (M^+; 99%, ^{130}Te), 260 (Te_2; bp), 138 ($M^+ - Te_2$; 69%), 110 (FC_6H_4N; 90%); IR (KBr) 3068, 3049, 1501, 1359, 1229, 1158, 1135, 1108, 1052, 990 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.45 (4H, br s), 7.12–7.27 (4H, m); ^{13}C NMR (DMSO-d_6) δ 38.2 (t), 115.6 (dd, $J_{C\text{–}F} = 21.9$ Hz, $J_{C\text{–}H} = 21.7$ Hz), 119.4 (dd, $J_{C\text{–}F} = 8.2$ Hz, $J_{C\text{–}H} = 4.0$ Hz), 139.5 (s), 158.9 (d, $J_{C\text{–}F} = 240.0$ Hz). Calcd for $C_8H_8FNTe_2$: C, 24.49; H, 2.06; N, 3.57%. Found: C, 24.30; H, 2.34; N, 3.63%.

General Procedure for Oxidation of 1,5,3,7-Dithiadiazocane (1) Using Bromine in the Presence of Elemental Sulfur. A carbon tetrachloride solution (20 mL) of bromine (Br_2, 196 mg, 1.10 mmol) was added dropwise to a dichloromethane solution (130 mL) of 1,5,3,7-dithiadiazocane **1** (1.50 mmol) and elemental sulfur (144 mg, 0.56 mmol) at −78 °C under an argon atmosphere, and the reaction mixture was stirred at −78 °C for 10–60 min. The reaction was quenched with an excess amount of 10% aqueous NaOH solution, and was extracted with dichloromethane. The organic layer was washed with water and was dried over anhydrous sodium sulfate powder. After removing the solvent in vacuo, the residual yellow solid was subjected to chromatographic purification using silica gel to obtain 1,2,3,4,5,7-pentathiazocane **9** and perhydro-1,3,5-thiadiazine **8**. Recrystallization from ethanol gave pure 1,2,3,4,5,7-pentathiazocane **9** as pale yellow solids.

9a (R = C_6H_5): Pale yellow needles, mp 123.0–124.0 °C (dec.); MS (*m*/*z*) 247 ($M^+ - S$; 4%), 215 ($M^+ - S_2$; 5%), 183 ($M^+ - S_3$; 68%), 119 ($M^+ - S_5$; 80%), 91 (bp); IR (KBr) 3060, 3039, 3029, 1596, 1503, 1440, 1365, 1347, 1270, 1238 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.79 (2H, d, $J = 15.0$ Hz), 5.70 (2H, d, $J = 15.0$ Hz), 6.60–7.50 (5H, m); ^{13}C NMR ($CDCl_3$) δ 65.9 (dd), 113.8 (d), 120.5 (d), 129.9 (d), 141.9 (s). Calcd for $C_8H_9NS_5$: C, 34.38; H, 3.25; N, 5.10; S, 57.37%. Found: C, 34.33; H, 3.15; N, 5.03; S, 56.93%.

9b (R = *p*-ClC_6H_4): Pale yellow needles, mp 128.7–129.5 °C; MS (*m*/*z*) 313 (M^+; 4%), 281 ($M^+ - S$; 1%), 250 ($M^+ - S_2$; 6%), 217 ($M^+ - S_3$; 21%), 64 (S_2; bp); IR (KBr) 2930, 2366, 1863, 1597, 1495, 1441, 1370, 1326, 1268, 1238, 890, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.79 (2H, d, $J = 15.0$ Hz), 5.62 (2H, d, $J = 15.0$ Hz), 6.67 (2H, d, $J = 9.0$ Hz), 7.30 (2H, d, $J = 9.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 65.6 (d), 114.9 (d), 125.8 (d), 129.7 (d), 140.4 (s). Calcd for $C_8H_8ClNS_5$: C, 30.61; H, 2.57; N, 4.40%. Found: C, 30.53; H, 2.65; N, 4.40%.

9c (R = *p*-$CH_3OC_6H_4$): Pale yellow needles, mp 91.2–91.8 °C (dec.); MS (*m*/*z*) 277 ($M^+ - S$; 0.2%), 245 ($M^+ - S_2$; 2%), 213 ($M^+ - S_3$; 68%), 135 ($M^+ - S_5$; 90%), 64 (S_2; bp); IR (KBr) 3047, 2992, 2948, 2920, 2827, 1578, 1511, 1436, 1364, 1274, 1249, 1207, 1186, 1143, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (3H, s), 4.79 (2H, d, $J = 15.0$ Hz), 5.66 (2H, d, $J = 15.0$ Hz), 6.74 (2H, d, $J = 9.1$ Hz), 6.92 (2H, d, $J = 9.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 55.6 (q), 66.7 (d), 115.4 (d), 136.0 (d), 154.2 (s). Calcd for $C_9H_{11}NOS_5$: C, 34.93; H, 3.58; N, 4.53%. Found: C, 35.21; H, 3.57; N, 4.40%.

9d (R = *p*-$CH_3C_6H_4$): Pale yellow needles, mp 135.0–136.0 °C (dec.); MS (*m*/*z*) 293 (M^+; 0.1%), 261 ($M^+ - S$; 0.1%), 229 ($M^+ - S_2$; 15%), 197 ($M^+ - S_3$; 39%), 133 ($M^+ - S_5$; 45%), 105 (bp), 64 (S_2; 66); IR (KBr) 2917, 2852, 1616, 1577, 1519, 1441, 1367, 1267, 1235, 1206, 1195, 1152, 1032, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.29 (3H, s), 4.78 (2H, d, $J = 15.0$ Hz), 5.68 (2H, d, $J = 15.0$ Hz), 6.69 (2H, d, $J = 8.3$ Hz), 7.15 (2H, d, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.2 (q), 66.1 (dd), 113.8 (d), 130.0 (d), 130.2 (d), 130.6 (s). Calcd for $C_9H_{11}NS_5$: C, 36.83; H, 3.78; N, 4.77%. Found: C, 36.80; H, 3.76, N, 4.60%.

10a (R = C_6H_5): Colorless prisms, mp 103.0–105.0 °C (lit.[88] 105 °C); IR (KBr) 3025, 2918, 1600, 1579, 1497, 1446, 1351 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.93 (4H, s), 5.17 (2H, s), 6.78–7.15 (10H, m).

10b (R = *p*-ClC_6H_4): Colorless prisms, mp 149.7–150.6 °C; MS (*m*/*z*) 324 (M^+; 11%), 185 ($M^+ - CH_2{=}NC_6H_4Cl$; 32%), 139 ($CH_2{=}NC_6H_4Cl$; bp), 111 (C_6H_4Cl; 31%); IR (KBr) 2927, 1600, 1589, 1492, 1234, 940, 562 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.88 (4H, s), 5.11 (2H, s), 6.88 (4H, d, $J = 9.0$ Hz), 7.08 (4H, d, $J = 9.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 55.8 (s), 69.9 (s), 119.1 (d), 125.8

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for **5c** and **6e**

Bond lengths for **5c**		Bond angles for **5c**		Bond length for **6e**		Bond angles for **6e**	
Se(1)–Se(2)	2.331(2)	Se(2)–Se(1)–C(1)	88.9(4)	Te(1)–Te(2)	2.7561(8)	Te(2)–Te(1)–C(1)	83.8(2)
Se(1)–C(1)	2.05(1)	Se(1)–Se(2)–C(2)	90.2(3)	Te(1)–C(1)	2.263(8)	Te(1)–Te(2)–C(2)	85.9(2)
Se(2)–C(2)	2.07(1)	C(1)–N(3)–C(2)	112(1)	Te(2)–C(2)	2.254(9)	C(1)–N(1)–C(2)	113.3(7)
N(3)–C(1)	1.43(1)	C(1)–N(3)–C(60)	116.9(9)	N(1)–C(1)	1.404(9)	Te(1)–C(1)–N(1)	112.2(5)
N(3)–C(2)	1.37(1)	C(2)–N(3)–C(60)	119(1)	N(1)–C(2)	1.41(1)	Te(2)–C(2)–N(1)	110.7(5)
		Se(1)–C(1)–N(3)	108.2(7)	N(1)–C(3)	1.422(8)	N(1)–C(3)–C(4)	120.9(6)
		Se(2)–C(2)–N(3)	110.3(7)			N(1)–C(3)–C(8)	120.9(7)

(s), 128.9 (d), 145.9 (s). Calcd for $C_{15}H_{14}Cl_2N_2S$: C, 55.39; H, 4.34; N, 8.61%. Found: C, 55.21; H, 4.32; N, 8.57%.

10d (R = *p*-$CH_3C_6H_4$): Colorless prisms, mp 96.1–97.6 °C; MS (*m/z*) 284 (M^+; 16%), 165 ($M^+ - CH_2{=}NC_6H_4CH_3$; 18%), 119 ($CH_2{=}NC_6H_4CH_3$; bp), 91 ($C_6H_4CH_3$; 63%); IR (KBr) 2916, 1617, 1573, 1449, 1357, 1224, 1068, 928, 562 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (3H, s), 4.87 (4H, s), 5.04 (2H, s), 6.89 (4H, d, $J = 8.5$ Hz), 6.98 (4H, d, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.4 (q), 54.3 (s), 70.1 (s), 118.0 (d), 129.5 (d), 129.8 (s), 145.4 (s). Calcd for $C_{17}H_{20}N_2S$: C, 71.79; H, 7.09; N, 9.85%. Found: C, 71.84; H, 7.09; N, 9.65%.

11a (R = C_6H_5): Colorless solid. Calcd for $C_8H_9NS_5$: C, 52.42; H, 4.95; N, 7.64%. Found: C, 52.97; H, 5.27; N, 7.87%.

X-ray Crystallographic Analysis of 5c. A reddish brown prism of $C_9H_{11}NOSe_2$ having approximate dimensions of $0.25 \times 0.10 \times 0.25$ mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer, equipped with a rotating anode (45 kV, 200 mA), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The crystal data are as follows: $a = 5.787(5)$ Å, $b = 9.993(3)$ Å, $c = 17.878(7)$ Å, $\beta = 94.68(5)°$, $V = 1027(1)$ Å^3, the space group $P2_1/c$ (No. 14), $Z = 4$, $D_{calcd} = 1.985$ g cm^{-3}, μ(Mo Kα) $= 70.84$ cm^{-1}. The ω-2θ scan mode with a scan rate of 8° min^{-1} (ω) was employed with a scan range of $1.00 + 0.30 \tan\theta$. A total of unique 2889 reflections within $2\theta = 55°$ were collected. The structure was solved by a direct method and refined by a full-matrix least-square method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms found in the successive D-Fourier map were refined with the riding mode. The final cycle of refinement was carried out using 1389 observed reflections within $I_o > 1.2\sigma(I_o)$ and 132 variable parameters converged to the final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ value of 0.039 and $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w {F_o}^2]^{1/2}$ of 0.056 (Tables 4 and 6).

X-ray Crystallographic Analysis of 6e. A dark plate crystal of $C_8H_8FNTe_2$ having approximate dimensions of $0.05 \times 0.10 \times 0.20$ mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku/MSC CCD diffractometer (50 kV, 40 mA), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The crystal data are as follows: $a = 18.699(5)$ Å, $c = 11.820(5)$ Å, $V = 4132(2)$ Å^3. the space group $I4_1/a$ (No. 88), $Z = 16$, $D_{calcd} = 2.522$ g cm^{-3}, μ(Mo Kα) $= 56.10$ cm^{-1}. A sweep of data was done using ω oscillation mode. A total of 13898 reflections within $2\theta = 55°$ were collected, of which 2434 were unique ($R_{int} = 0.034$). The structure was solved by a direct method and refined by a full-matrix least-square method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms found in the successive D-Fourier map were refined isotropically. The final cycle of refinement was carried out using 1354 observed reflections within $I_o > 3.00\sigma(I_o)$ and 141 variable parameters converged to the final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ value of 0.027 and $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w {F_o}^2]^{1/2}$ of 0.027. The maximum and minimum peaks on the final difference Fourier map corresponds to 0.61 and -0.45 eÅ^{-1}, respectively (Tables 4 and 6). Crystallographic data have been deposited at the CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK, and the copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 157641 (via http://www.ccdc.cam.ac.uk/conts/retrieving.html or Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The data are also deposited as Document No. 06105 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The X-ray Crystallographic Analysis of 9a. A colorless prism of $C_8H_9NS_5$ having approximate dimensions of $0.30 \times 0.20 \times 0.20$ mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer, equipped with a rotating anode (40 kV, 180 mA), using graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å). The crystal data are as follows: $a = 13.533(3)$, $b = 4.7633(9)$, $c = 19.485(3)$ Å, $\beta = 110.15(1)°$, $V = 1179.1(4)$ Å^3, the space group $P2_1/c$ (No. 14), $Z = 4$, $D_{calcd} = 1.574$ g cm^{-3}, μ(Cu Kα) $= 87.29$ cm^{-1}. The ω-2θ scan mode with a scan rate of 4° min^{-1} (ω) was employed with a scan range of $1.30 + 0.30 \tan\theta$. A total of unique 2542 reflections within $2\theta = 125.7°$ were collected. The structure was solved by a direct method and refined by a full-matrix least-square method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms found in the successive D-Fourier map were refined isotropically. The final cycle of refinement was carried out using 1716 observed reflections within $I_o > 3.00\sigma(I_o)$ and 163 variable parameters converged to the final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ value of 0.065 and $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w {F_o}^2]^{1/2}$ of 0.067. The maximum and minimum peaks on the final difference Fourier map corresponds to 0.62 and -0.32 eÅ^{-1}, respectively (Tables 4 and 7).

Attempts for *m*CPBA or Peracid Oxidation of 1,2,3,4,5,7-Pentathiazocane 9a. A dichloromethane solution (100 mL) of 1,2,3,4,5,7-pentathiazocane **9a** (279 mg, 1.00 mmol) was treated with *m*CPBA (193 mg, 1.10 mmol) or acetic acid (66 mg, 1.1 mmol) and 34.5% aq. H_2O_2 solution (91 mg, 3.50 mmol) at rt, and then the mixture was refluxed for 1 h. The reaction was quenched with an excess amount of saturated aqueous Na_2SO_3 solution, and was extracted with dichloromethane. The organic layer was washed with saturated $NaHCO_3$ solution and with water and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, substrate **9a** (263 mg, 94% yield in both cases) was recovered.

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Table 7. Selected Bond Lengths (Å), Bond Angles (deg), Torsion Angles (deg), and Spacial Contacts (Å) for **9a**

Bond lengths/Å		Bond angles/deg		Torsion angles/deg		Spacial contacts/Å	
C(1)–S(1)	1.845(8)	S(2)–S(1)–C(1)	104.5(2)	S(1)–S(2)–S(3)–S(4)	−89.4(1)	S(1)–S(3)	3.289(2)
S(1)–S(2)	2.023(2)	S(1)–S(2)–S(3)	107.87(8)	S(1)–C(1)–N(1)–C(2)	104.0(4)	S(1)–S(4)	4.256(2)
S(2)–S(3)	2.046(2)	S(2)–S(3)–S(4)	107.03(10)	S(1)–C(1)–N(1)–C(3)	−72.1(5)	S(1)–S(5)	4.267(2)
S(3)–S(4)	2.046(2)	S(3)–S(4)–S(5)	108.26(9)	S(2)–S(1)–C(1)–N(1)	−99.1(4)	S(2)–S(4)	3.290(2)
S(4)–S(5)	2.032(2)	S(4)–S(5)–C(2)	104.4(2)	S(2)–S(3)–S(4)–S(5)	89.0(1)	S(2)–S(5)	4.264(2)
S(5)–C(2)	1.865(5)	C(1)–N(1)–C(2)	118.4(4)	S(3)–S(2)–S(1)–C(1)	92.1(2)	S(3)–S(5)	3.304(2)
C(2)–N(1)	1.409(6)	C(1)–N(1)–C(3)	120.0(4)	S(3)–S(4)–S(5)–C(2)	−91.9(2)		
C(1)–N(1)	1.424(5)	C(2)–N(1)–C(3)	121.5(3)	S(4)–S(5)–C(2)–N(1)	99.3(4)		
N(1)–C(3)	1.398(6)	S(1)–C(1)–N(1)	116.6(3)	S(3)–S(4)–S(5)–C(2)	−91.2(2)		
				S(4)–S(5)–C(2)–N(1)	99.3(4)		
				S(5)–C(2)–N(1)–C(1)	−104.3(4)		
				S(5)–C(2)–N(1)–C(3)	71.8(5)		

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