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Synthesis and Reactions of 2-Alkylidene-1,3,4-thiadiazolines and Their Selenium Analogues

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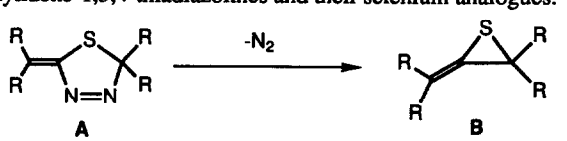
Abstract

2-Alkylidene-1,3,4-thiadiazoline **11a** gave thioketone **16** (X=S) and acetylene derivative **17** on thermolysis *via* thiocarbonyl ylide, quantitatively. Pyrolysis of selenium analogue gave similar results. Allyl substituted 2-alkylidene-1,3,4-thiadiazolines **11a** and **11b** resulted in the novel formation of thiiranimine derivatives **19a** and **19b** and bicyclo[3.1.0]thiahexane derivatives **20a** and **20b** *via* azathioallyl intermediates. Thiiranimine derivatives **19a** and **19b** were converted to 2-alkylidene-1,3,4-thiadiazolines **11a** and **11b** under acidic conditions.

Introduction

Thermolysis of 1,3,4-thiadiazolines and selenadiazolines[2] have been widely inspected as a useful synthetic route to a variety of hindered olefins and also as a method for generating thio- and selenocarbonyl ylides.[3] However, only a few reports have appeared on the thermolysis of 2-alkylidene-1,3,4-thiadiazolines[4] and that on their selenium analogues was very few. Thermal decomposition of 2-alkylidene-1,3,4-thiadiazoline (**A**) may be one of good approaches to produce allene episulfide (**B**). We have previously reported synthesis and reactions of 2-alkylidene-1,3,4-thiadiazolines and their selenium analogues.[4d] We present here the detailed product analysis and mechanism on thermolysis and photolysis of 2-alkylidene-1,3,4-thiadiazolines and their selenium analogues.

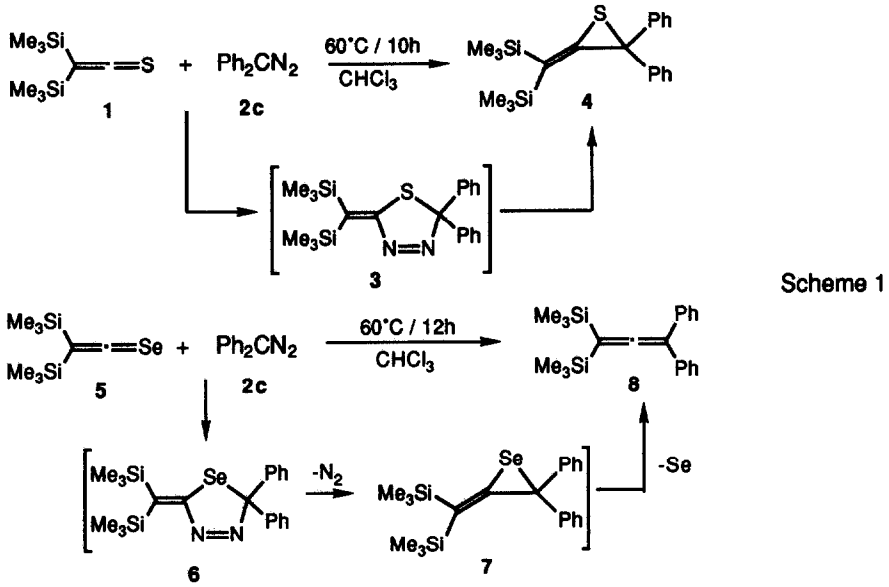


A **B**

Results and Discussions

Reactions of Thioketenes or Selenoketenes with Diazo Compounds; Syntheses of 2-Alkylidene-1,3,4-chalcogenadiazolines.

Bis(trimethylsilyl)thioketene **1**[5] reacted with diphenyldiazomethane **2c** at 60 °C to yield allene episulfide **4** *via* 2-alkylidene-1,3,4-thiadiazoline **3** in 53% yield.[4c] The selenium analogue did not afford an expected allene episelenide **7** but gave the corresponding allene **8** in 60% yield by two-fold extrusion of nitrogen and selenium. (Scheme 1) In contrast to the bis(trimethylsilyl)alkylidene systems,



Scheme 1

2-alkylidene-1,3,4-thiadiazolines **11** and their selenium analogues **13** were successfully synthesized by cycloaddition of diazo compounds **2** with thioketene **9**[6a] or selenoketene **10**[6b] in good yields. (Scheme 2 and Table 1) The reaction of thioketene **9** with diphenyldiazomethane **2c** did not give 2-alkylidene-1,3,4-thiadiazoline **11c**, but allene episulfide **12c** was obtained in 30% yield by extrusion of nitrogen under the applied conditions.[7] The configuration of **11a** was determined by ^1H, ^{13}C NMR and X-ray structure analysis. The molecular structure and configuration of **11a** was unequivocally established by a single-crystal X-ray diffraction structure analysis. An ORTEP drawing of **11a** is shown in Figure I. Selected interatomic distances and angles are listed in Table 2. Interatomic distances of thiadiazoline ring are : 1S—1C = 1.7705, 1S—8C = 1.8123, 8C—1N = 1.4835, 1C—2N = 1.4362, 1N—2N = 1.2292 Å. The distance of 1S—8C is longer than 1S—1C, which is due to the conjugation between lone pair on sulfur atom and olefin moiety. Both E and Z forms of thiadiazolines **11b** (**E** and **Z**) were formed in the reaction of thioketene **9** and di-*tert*-butyldiazomethane **2b**. The chemical shifts of two sets of olefin signals in **11a** are close to those of **11b**(**E**) in ^1H and ^{13}C NMR spectra. These results suggest that the diazoalkanes are easy to approach to thiocarbonyl moiety of **9** on opposite side of dimethylallyl group which is bulkier than trimethylsilyl group. The objective of using dimethylallyl substituted thioketene **9** is intramolecular trapping of intermediates generated from thermolysis or photolysis of 2-alkylidene-1,3,4-thiadiazolines. The 2-alkylidene-1,3,4-selenadiazolines **13a-c** were prepared by the reaction of selenoketene **10** with diazo compounds **2a-c** under milder conditions compared with the sulfur analogues. (Table 1) Higher reactivity of selenoketene **10** than that of **9** made it possible to isolate 2-alkylidene-1,3,4-selenadiazoline **13c** without denitrogenation under mild conditions.

Scheme 2

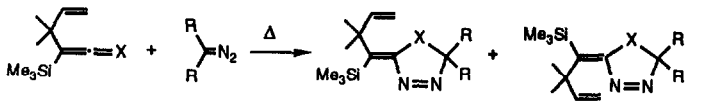
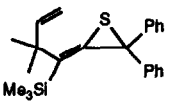
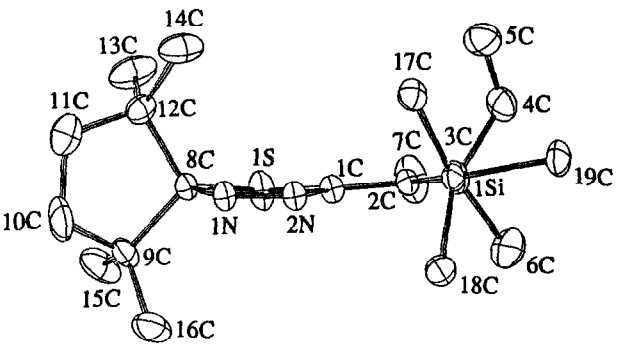


Table 1. Syntheses of 2-Alkylidene-1,3,4-thiadiazolines and Their Selenium Analogues

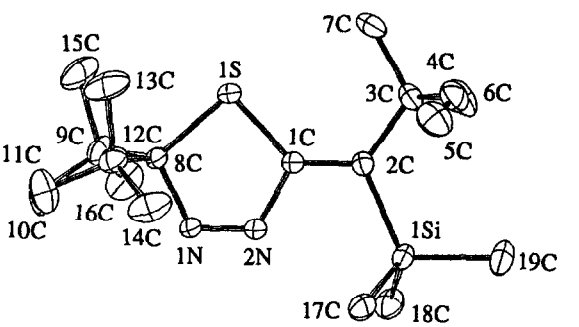
X		R, R	reaction conditions	isolated yields (E+Z)
S	a		benzene / reflux / 9h	44%
	b	^{t}Bu x 2	benzene / reflux / 13h	79%
	c	Ph x 2	$ClCH_2CH_2Cl$ / 80°C/15h	**
Se	a		Et_2O / reflux / 12h	56%
	b	^{t}Bu x 2	Et_2O / reflux / 12h	60%
	c	Ph x 2	Et_2O / r.t. / 3 days	36%

** 

12c
was isolated in 30% yield.



(a)



(b)

Figure I. ORTEP drawing of **11a**, (a) side view, (b) top view.

Table 2. Selected Bond Distances and Angles of **11a**.

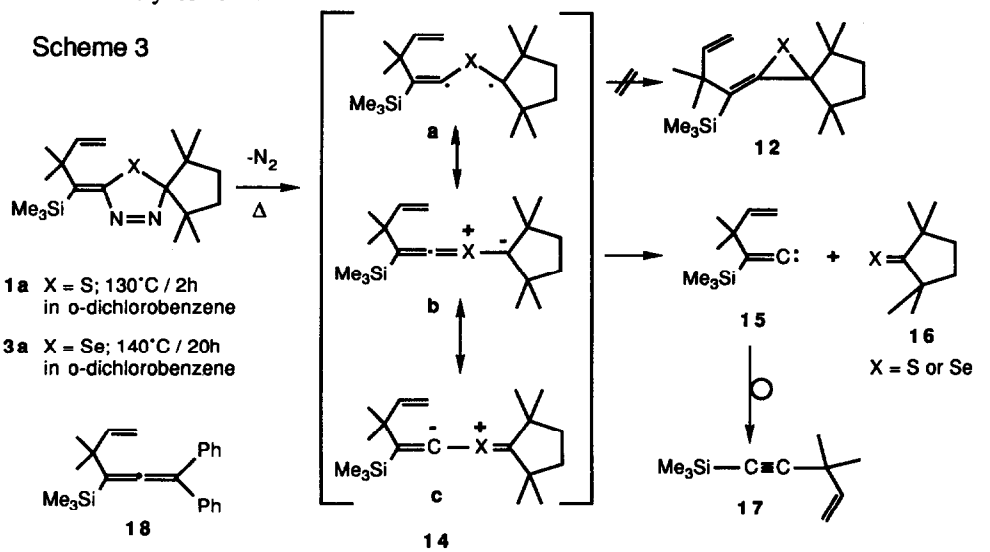
1S—1C	1.7705	1S—8C	1.8123
1N—2N	1.2292	1N—8C	1.4835
1C—2C	1.3352	1C—2N	1.4362
2C—3C	1.5396	3C—4C	1.4914
3C—6C	1.5492	3C—7C	1.5458
4C—5C	1.2499	8C—9C	1.5608
9C—10C	1.5344	9C—15C	1.5316
9C—16C	1.5028	10C—11C	1.4577
11C—12C	1.5150	12C—8C	1.5601
12C—13C	1.5382	12C—14C	1.5204
1Si—2C	1.9233	1Si—17C	1.8623
1Si—18C	1.8641	1Si—19C	1.8842
1S—1C—2C	133.80	1S—1C—2N	108.20
1S—8C—9C	114.61	1S—8C—12C	115.80
1N—8C—1S	104.99	1N—8C—9C	107.30
1N—8C—12C	107.25	2N—1C—2C	118.00
2N—1N—8C	117.20	1Si—2C—1C	114.70
1Si—2C—3C	120.48	1C—1S—8C	91.47
1C—2N—1N	117.27	1C—2C—3C	124.81
2C—1Si—17C	109.89	2C—1Si—18C	110.40
2C—1Si—19C	114.06	2C—3C—4C	111.33
2C—3C—6C	107.50	2C—3C—7C	114.94
3C—4C—5C	126.54	4C—3C—6C	110.31
4C—3C—7C	105.91	6C—3C—7C	106.74
8C—9C—10C	100.29	8C—9C—15C	112.09
8C—9C—16C	112.79	8C—12C—13C	112.12
8C—12C—14C	112.11	9C—10C—11C	108.77
10C—9C—15C	111.45	10C—9C—16C	110.93
10C—11C—12C	110.39	11C—12C—8C	102.42
11C—12C—13C	112.91	11C—12C—14C	111.42
12C—8C—9C	106.39	13C—12C—14C	106.02
15C—9C—16C	109.10	17C—1Si—18C	111.47
17C—1Si—19C	105.06	18C—1Si—19C	105.82

Thermal Decomposition of 2-Alkylidene-1,3,4-thiadiazolines and Their Selenium Analogues.

When **11a** was heated in o-dichlorobenzene at 130 °C for 2 h, the thioketone **16** (X=S) and dimethylallyl(trimethylsilyl)acetylene **17** were obtained quantitatively without any formation of the expected allene episulfide **12a** (X=S) as shown in Scheme 3. Monitoring of this reaction by ^{1}H NMR failed to detect allene episulfide **12a** (X=S), thioketene **9**, diazo compound, or the corresponding azine except **16** and **17**. Thermolysis of the selenium analogue **13a** also gave selenoketone **16** (X=Se) and **17**. Guziec, Jr. et al.[2a] reported that pyrolysis of 1,3,4-selenadiazolines affords the corresponding selones and retrocyclization products. These results suggest that carbenes or carbenoid compounds are not involved as intermediates, since in no cases they have been able to trap unrearranged products by intermolecular reactions. We have obtained acetylene derivative **17**, the formation of which suggests the intermediacy of alkylidene carbene in pyrolysis of chalcogenadiazolines **11a** and **13a**.

A plausible mechanism is as follows. The initial intermediate **14a**, generated by thermal denitrogenation of **11a** or **13a** should resonate to the ylides **14b** and **14c**. The silylacetylene **17** might be produced by the carbon-chalcogen bond cleavage of **14c** leading to the formation of **16** (X=S or Se) and the alkylidenecarbene **15** followed by the ready migration of trimethylsilyl group.[8] Since the formation of acetylene from vinylidene is strongly exothermic,[9] **15** did not undergo recombination with **16** but exclusively isomerized into **17**.

Scheme 3



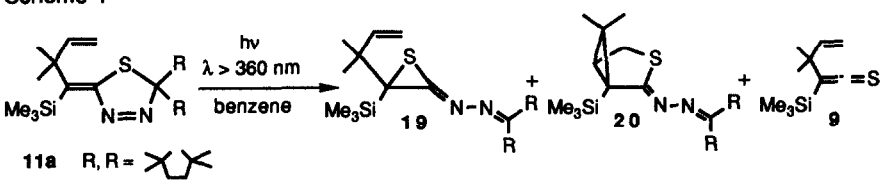
The selective carbon-chalcogen bond cleavage and the lack of ring closure product **12a** (X=S) or its selenium analogue, which is in sharp contrast to the facile allene episulfide formation from **1** and **2c** *via* **3**, are probably due to the steric hindrance of the bulky substituents in these systems. An analogous carbene formation has been already described in the thermolysis of 1,3,4-oxadiazoline derivatives, though the reaction mechanism was interpreted in terms of a favorable carbonyl compound formation.[10]

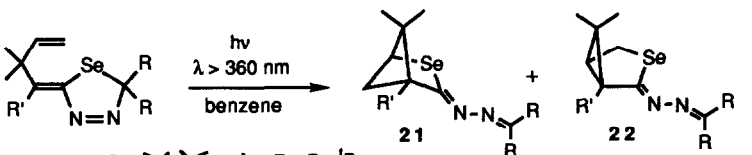
On the other hand, thermolysis of **11b** gave a complex mixture at 140 °C for 3 h. When **13c** was pyrolyzed at 280-300 °C in a stream of nitrogen, the corresponding allene **18** was yielded quantitatively.

Photolysis of 2-Alkylidene-1,3,4-thiadiazolines and Their Selenium Analogues.

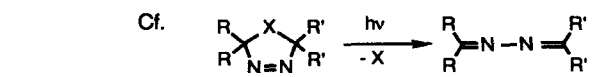
Irradiation of a benzene solution of **11a** with a medium pressure mercury lamp through a phenanthrene filter solution at room temperature for 10 min gave thiiranimine derivative **19a** in 51% yield along with 15% of bicyclo[3.1.0]thiahexane derivative **20a**. Compound **11b** gave thioketene **9**, **19b**, and **20b** in 11, 19 and 29% yields, respectively. The structures of **19a** (**b**) and **20a** (**b**) were confirmed by ^1H and ^{13}C NMR, mass and exact mass spectroscopy. The ^{13}C NMR spectra of **19a** (**b**) and **20a** (**b**) suggest azine skeleton, and thus two couples of imine carbon resonance appeared at 186.8 (178.3)(s) and 155.8 (155.2)(s) for **19a** (**b**) and 198.7 (196.3) (s) and 196.8 (189.6) (s) for **20a** (**b**). The photochemical reactions of **13a-d** are more complicated, however, bicyclic compounds **21** and/or **22** were obtained in low yields after careful chromatographic separation. The structures of **21** and **22** were determined by ^1H and ^{13}C NMR.

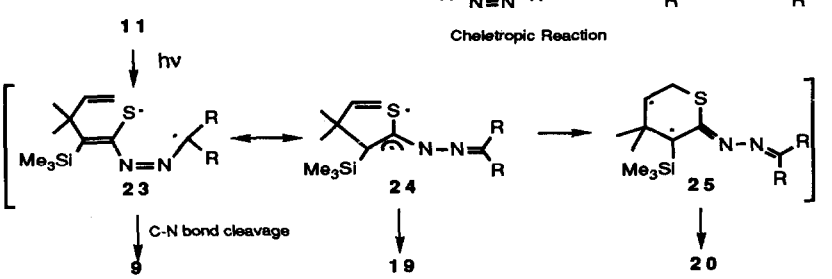
Scheme 4

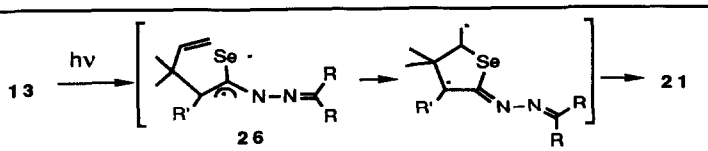




Scheme 5





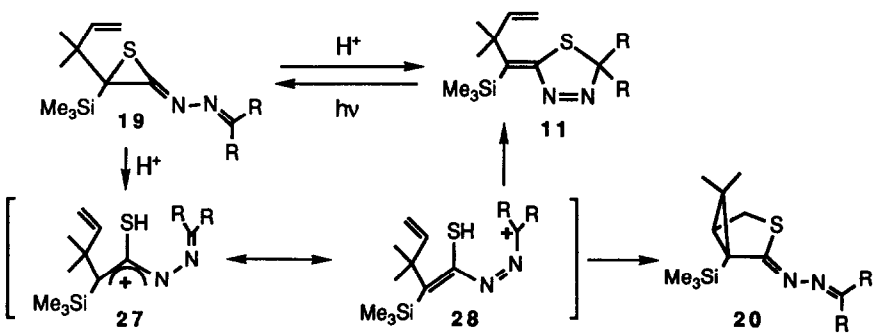


The conceivable mechanism is illustrated in Scheme 5. At first the biradical intermediate **23** might be generated by the cleavage of C-S bond of **11**, opposite to the exocyclic double bond, followed by three competitive routes : (1) C-N bond fission leading to **9**, (2) new C-S bond formation to afford **19** *via* azathioallyl intermediate **24**, and (3) formation of bicyclic compound **20** by the intramolecular cyclization of **25**. The competitive formation of **21** and **22** in the case of **13** is also rationalized by the intramolecular trapping of the alternative biradical intermediate **26**. It is noteworthy that the reaction mode of the 2-alkylidene-1,3,4-chalcogenadiazolines thus described is considerably different from that of the concerted cheletropic reaction in the case of simple 1,3,4-thiadiazolines.[3a]

Acid Catalyzed Isomerization of Thiiranimine Derivatives **19**.

The addition of acid causes allene episulfides to isomerize to some different isomers.[7,11] Allyl substituted allene episulfides were also isomerized to form cyclopentenethione by treatment with a catalytic amount of BF_3•Et_2O.[7] Phenyl substituted thiiranimine isomerizes to benzothiophene upon warming, as reported by L'abbé.[12] Thiiranimine **19a** here obtained was found to undergo quantitative isomerization to **11a** by a catalytic amount of trifluoroacetic acid. Compound **19b** also produced **11b** as the major product together with a trace amount of **20b**. This interesting acid catalyzed ring transformation can be interpreted as the result of intramolecular reaction *via* the azathioallyl cation **27**. It is anticipated these results are due to resonance effect between azathioallyl cation and azine skeleton. Thus the predominant formation of **11** over **20** is well explained by the preferential nucleophilic attack of sulfur atom on the stabilized cationic reaction center by the two alkyl groups in the resonance structure **28**.

Scheme 6



19				products	
R,R	solv.	reaction conditions	acid	11	20
a)	CCl_4	r.t. / 3 h	CF_3CO_2H	quant.	---
	CCl_4	r.t. / 3 h	none	no reaction	
b) ^{t}Bux2	C_6D_6	r.t. / 10 min.	CF_3CO_2H	main	trace

Experimental Section

General Data.

Reagent-grade solvents were distilled from sodium benzophenone ketyl prior to use. Bis(trimethylsilyl)thioketene **1**,[5] bis(trimethylsilyl)selenoketene **5**[13], 3,3-dimethylallyl(trimethylsilyl)-thioketene **9**,[6a] 3,3-dimethylallyl(trimethylsilyl)selenoketene **10**,[6b] diazo-2,2,5,5-tetramethylcyclopentane **2a**,[2b] di-*tert*-butyldiazomethane **2b**,[14] and diphenyldiazomethane **2c**[15] were prepared by the published procedures. All reactions were performed under an argon atmosphere unless otherwise specified. Infrared spectra were recorded on a Hitachi 260-50 infrared spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM500 or a JEOL PMX 60SI spectrometer operating at 500 and 60 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker AM500 spectrometer operating at 125 MHz. UV-visible spectra were recorded on a JASCO Ubest-50. Melting points are uncorrected. Elemental analyses were carried out by the Chemical Analytical Center of University of Tsukuba. Mass spectra and high resolution mass spectra were obtained on a JEOL JMS SX102A mass spectrometer.

Reaction of Bis(trimethylsilyl)selenoketene (**5**) with Diphenyldiazomethane (**2c**).

A solution of bis(trimethylsilyl)selenoketene (94 mg, 0.37 mmol) and diphenyldiazomethane (82 mg, 0.42 mmol) in 0.4 mL of $CDCl_3$ was heated at 60 °C for 12 h. ^{1}H NMR analysis of this mixture demonstrated the production of the allene **8**. After removal of the solvent *in vacuo*, the residue was separated by preparative TLC (SiO_2 / eluent; hexane). Evaporation of the solvent gave **8** (75 mg, 60%), **8**: a colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.08 (18 H, s), 7.1-7.6 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 0.45 (q), 93.0 (s), 96.7 (s), 121.56 (d), 127.5 (d), 128.3 (d), 137.6 (s), 209.2 (s); IR (CCl_4) ν 1895 cm^{-1}; MS m/e 336 (M^+, 29%), 263 (6), 248 (69), 73 (100); HRMS calcd for $C_{21}H_{28}Si_2$ 336.1728, found 336.1726.

Synthesis of 2-[2',2'-Dimethyl-1'-trimethylsilyl-3'-butenylidene]-5-spiro[1',1',3',3'-tetramethylcyclopentyll-Δ^3-1,3,4-thiadiazoline (**11a**).

A benzene solution (5 mL) of thioketene **9** (288 mg, 1.45 mmol) and 2-diazo-1,1,3,3-tetramethylcyclopentane **2a** (205 mg, 1.34 mmol) was refluxed for 9 h under dry nitrogen. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent; hexane). Removal of the hexane gave **11a** (114 mg, 44% yield based on consumed **9**) and unreacted thioketene **9** (125 mg). **11a** was recrystallized from hexane, **11a**: pale yellow crystals; mp 67.5—68.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.30 (9 H, s), 0.67 (6 H, s), 1.13 (6 H, s), 1.42 (6 H, s), 1.68 (2 H, dd, J = 13, 6 Hz), 2.21 (2 H, dd, J = 13, 6 Hz), 5.02 (1 H, d, J = 17 Hz), 5.05 (1 H, d, J = 10.5 Hz), 6.06 (1 H, dd, J = 10.5, 17 Hz); ^{13}C NMR ($CDCl_3$) δ 4.7 (q), 24.7 (q), 28.3 (q), 29.9 (q), 38.2 (t), 43.3 (s), 48.1 (s), 112.7 (t), 125.3 (s), 147.8 (d), 150.8 (s), 165.1 (s); UV (cyclohexane) λmax 348 nm (log ε = 3.82); MS m/e 350 (M^+, 6%), 335 (18), 277 (100), 73 (11); HRMS calcd for $C_{19}H_{34}N_2SSi$ 350.2211, found 350.2206. Anal. Calcd for $C_{19}H_{34}N_2SSi$: C, 65.08; H, 9.77; N, 7.99. Found: C, 64.75; H, 9.76; N, 7.85.

Synthesis of 2-[2',2'-Dimethyl-1'-trimethylsilyl-3'-butenylidene]-5,5-di-*tert*-butyl-Δ^3-1,3,4-thiadiazoline (**11b**).

A solution of thioketene **9** (400 mg, 2.20 mmol) and di-*tert* -butyldiazomethane **2b** (160 mg, 1.03 mmol) in 2 mL of benzene was refluxed for 13 h. The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography (eluent; hexane). A mixture of E and Z form of **11b** (775 mg) was obtained in 79% yield (E : Z = 10:1), **11b** (E): pale yellow crystals; mp 74.5-77.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.30 (9 H, s), 1.13 (18 H, s), 1.38 (6 H, s), 4.98 (1 H, d, J = 17 Hz), 5.02 (1 H, d, J = 10 Hz), 6.03 (1 H, dd, J = 17, 10 Hz); ^{13}C NMR ($CDCl_3$) δ 4.8 (q), 28.2 (q), 29.8 (q), 43.3 (s), 43.4 (s), 112.7 (t), 126.5 (s), 147.8 (d), 151.0 (s), 165.8 (s); UV (cyclohexane) λmax 355 nm (ε 8740); MS m/e 352 (M^+); HRMS calcd for $C_{19}H_{36}N_2SiS$ 352.2368, found 352.2353. **11b** (Z); pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 0.34 (9 H, s), 1.13 (18 H, s), 1.54 (6 H, s), 4.89 (1 H, d, J = 17 Hz), 4.90 (1 H, d, J = 10 Hz), 6.19 (1 H, dd, J = 17, 10 Hz); ^{13}C NMR ($CDCl_3$) δ 2.0 (q), 29.8 (q), 32.1 (q), 43.5 (s), 46.6 (s), 110.6 (t), 125.7 (s), 141.3 (s), 150.8 (d), 166.9 (s); UV (cyclohexane) λmax 362 nm (ε 2300); MS m/e 352 (M^+).

Synthesis of 2-[2',2'-Dimethyl-1'-trimethylsilyl-3'-butenylidene]-5-spiro[1',1',3',3'-tetramethylcyclopentyl]-Δ^3-1,3,4-selenadiazoline (**13a**).

A solution of selenoketene **10** (260 mg, 1.06 mmol) and diazo compound **2a** (115 mg, 0.75 mmol) in 2 mL of dry ether was refluxed for 12 h. The solvent was removed *in vacuo* and the residue was purified by silica-gel column chromatography (eluent; hexane-CH_2Cl_2). Evaporation of the hexane gave pure **13a** (167 mg) in 56% yield, **13a**: pale yellow crystals; mp 56.0—56.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.27 (9 H, s), 0.60 (6 H, s), 1.13 (6 H, s), 1.35 (6 H, s), 1.87 (2 H, dd, J = 13, 6 Hz), 2.20 (2 H, dd, J = 13, 6 Hz), 5.04 (1 H, dd, J = 1, 11 Hz), 5.05 (1 H, dd, J = 1, 17 Hz), 6.08 (1 H, dd, J = 11, 17 Hz); ^{13}C NMR ($CDCl_3$) δ 4.8 (q), 29.9 (q), 27.5 (q), 31.6 (q), 38.4 (t), 43.3 (s), 48.7 (s), 113.5 (t), 129.0 (s), 147.7 (d), 158.6 (s), 163.2 (s); UV (cyclohexane) λmax 362 nm (ε = 3500); MS m/e 398 (M^+, 13%), 383 (26), 325 (100), 73 (50); HRMS calcd for $C_{19}H_{34}N_2SeSi$ 398.1654, found 398.1647.

Synthesis of 2-[2',2'-Dimethyl-1'-trimethylsilyl-3'-butenylidene]-5,5-di-*tert* -butyl-Δ^3-1,3,4-selanadiazoline (**13b**).

An ether solution (6 mL) of selenoketene **10** (900 mg, 3.65 mmol) and diazo compound **2b** (560 mg, 3.6 mmol) was refluxed for 12 h. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (eluent; hexane). Pure **13b** (500 mg, 60%) was given after evaporation, **13b**: pale yellow crystals; mp 60.1—60.7 °C; ^{1}H NMR($CDCl_3$) δ 0.32 (9 H, s), 1.17 (18 H, s), 1.36 (6 H, s), 5.06 (1 H, dd, J = 1, 17 Hz), 5.08 (1 H, dd, J = 1, 10 Hz), 6.08 (1 H, dd, J = 10, 17 Hz); ^{13}C NMR ($CDCl_3$) δ 4.9 (q), 27.5 (q), 30.7 (q), 43.3 (s), 43.6 (s), 113.4 (t), 131.8 (s), 147.6 (d), 159.1 (s), 163.7 (s); UV (cyclohexane) λmax 375 nm (ε = 3490); MS m/e 400 (M^+, 7%), 343 (20), 331 (15), 274 (49), 112 (100), 73 (79), 57 (100). Anal. Calcd for $C_{19}H_{36}N_2SeSi$: C, 57.12; H, 9.08; N, 7.01. Found: C, 57.23; H, 9.30; N, 6.94.

Synthesis of 2-[2',2'-Dimethyl-1'-trimethylsilyl-3'-butenylidene]-5,5-diphenyl-Δ^3-1,3,4-selanadiazoline (**13c**) and 2-[2',2'-Dimethyl-3'-butenylidene]-5,5-diphenyl-Δ^3-1,3,4-selanadiazoline (**13d**).

An mixture of selenoketene **10** (500 mg, 2.03 mmol) and diphenyldiazomethane **2c** (500 mg, 2.57 mmol) in 8 mL of ether was stirred at room temperature for 3 days. After removal of solvent, the residue was separated by HPLC (eluent; $CHCl_3$). Pure **13c** (321 mg, 36%) and **13d** (270 mg, 36%) were given, **13c**: a pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.47 (9 H, s), 1.47 (6 H, s), 5.21 (1 H, dd, J = 1, 18 Hz; 1 H, dd, J = 1, 10), 6.24 (1 H, dd, J = 10, 18 Hz), 7.35 (10 H, s); ^{13}C NMR ($CDCl_3$) δ 4.8 (q), 27.0 (q), 43.7 (s), 114.5 (t), 127.3 (d), 127.4 (d), 127.5 (d), 127.75 (d), 127.86 (d), 127.95 (s), 128.32 (d), 128.35 (d), 128.4 (d), 142.3 (s), 143.2 (s), 147.0 (d), 163.0 (s); UV (cyclohexane) λmax 373 nm (ε = 3900); MS m/e 440 (M^+, 3%), 180 (34), 73 (100); HRMS calcd for $C_{23}H_{28}N_2SeSi$ 440.1186, found 440.1217.

For **13d**: pale yellow crystals; mp 67.0—68.0 °C; ^1H NMR ($CDCl_3$) δ 1.30 (6 H, s), 5.13 (1 H, dd, J = 1, 10 Hz), 5.16 (1 H, dd, J = 1, 18 Hz), 5.98 (1 H, dd, J = 10, 18 Hz), 7.29 (1 H, s), 7.0-7.3 (10H, br s); ^{13}C NMR ($CDCl_3$) δ 26.4 (q), 38.7 (s), 114.3 (t), 118.4 (s), 127.8 (d), 128.4 (d), 128.8 (d), 142.7 (s), 143.2 (d), 145.7 (d), 160.7 (s); UV (cyclohexane) λmax 348 nm (ε = 10400); MS m/e 368 (M^+, 8%), 340 (23), 180 (100).

Thermolysis of **11a** and **13a**.

An *o*-dichlorobenzene (0.6 mL) solution of **11a** (60 mg) in an NMR tube was heated at 130 °C for 2 h. ^1H NMR analysis demonstrated quantitative conversion of **11a** to thioketone **16** (X=S) and trimethylsilylacetylene derivative **17**. **16** and **17** were separated by preparative TLC (eluent; hexane).

For **16** (X=S): an orange oil; ^1H NMR ($CDCl_3$) δ 1.13 (12 H, s), 1.87 (4 H, s); MS m/e 156 (M^+).

For **16** (X=Se)[16]: a blue oil; ^1H NMR ($CDCl_3$) δ 1.21 (12 H, s), 1.93 (4 H, s); MS m/e 204 (M^+).

For **17**: a colorless oil; MS m/e 166 (M^+).

Thermolysis of **11b**.

When an *o*-dichlorobenzene (0.4 mL) solution of **11b** in an NMR tube was heated at 140 °C for 3 h, **11b** was completely consumed and a complex mixture was obtained. Allene episulfide, thioketone, acetylene derivatives were not detected by ^1H NMR.

Pyrolysis of **13c**.

The apparatus for pyrolysis consisted of a 28 cm x 1 cm Pyrex tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber cap for syringe introduction of the sample and a nitrogen inlet. The pyrolysis tube was maintained at 280—300 °C, and nitrogen flow was ca. 20 ml/min. The sample was introduced drop by drop using a syringe. The pyrolysates were collected in a receiver cooled by a dry ice-MeOH bath. A benzene solution (70 mL) of **13c** (100 mg) was pyrolyzed at 280—300 °C under flowing nitrogen. Separation of the reaction mixture by preparative TLC gave the corresponding allene **18**, a colorless solid; ^1H NMR ($CDCl_3$) δ 0.16 (9 H, s), 1.29 (6 H, s), 4.96 (1 H, d, J = 10 Hz), 5.02 (1 H, d, 17 Hz), 5.97 (1 H, dd, J = 10, 17 Hz), 7.2-7.6 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 1.24 (q), 28.6 (q), 42.0 (s), 105.9 (s), 109.3 (s), 110.8 (t), 126.3 (d), 127.8 (d),

128.4 (d), 137.6 (s), 147.8 (d), 205.8 (s); MS m/e 332 (M^+); IR (CCl_4) ν 1900 cm^{-1}; HRMS calcd for $C_{23}H_{28}Si$ 332.1959, found 332.1943.

Photolysis of **11a-b**,**13a-c**, and **13d**.

A typical experimental procedure for the photolysis of **11a** is described. A benzene solution (40 mL) of **11a** (50 mg, 0.14 mmol) was irradiated with a medium pressure mercury lamp through a phenanthrene filter solution (phenanthrene/MeOH = 5 g/l) for 10 min at room temperature. This manipulation was repeated 3 times, and three reaction mixtures were combined, and evaporated. Separation of the residue by preparative TLC (silica gel, CH_2Cl_2/hexane = 3/4) gave **19a** (76 mg, 51%) and **20a** (23 mg, 15%). The starting materials and product distributions are described below. **11b** gave **19b** (19%), **20b** (29%), and **9** (11%). **13a** yielded **21a** (8%) and **22a** (4%). **13b**, **13c**, and **13d** afforded **21b** (5%), **21c** (14%), and **21d** (8%), respectively. **19a**: a colorless oil; ^1H NMR ($CDCl_3$) δ 0.17 (9 H, s), 1.13, 1.16, 1.17, 1.20, 1.32, 1.34 (each 3 H, s), 1.64 (4 H, s), 5.07 (1 H, d, J = 14 Hz), 5.15 (1 H, d, J = 17 Hz), 6.00 (1 H, dd, J = 14, 17 Hz); ^{13}C NMR ($CDCl_3$) δ 0.2 (q), 24.9 (q), 25.5 (q), 26.3 (q), 26.6 (q), 27.8 (q), 27.9 (q), 37.4 (t), 39.7 (t), 41.7 (s), 44.3 (s), 44.5 (s), 45.5 (s), 112.9 (t), 144.7 (d), 155.8 (s), 186.8 (s); MS m/e 350 (M^+, 17%), 335 (6), 295 (25), 281 (58), 186 (49), 138 (34), 114 (44), 73 (100), 69 (69); HRMS calcd for $C_{19}H_{34}N_2SSi$ 350.2211, found 350.2194. **20a**: white crystals; mp 114.0—114.5 °C; ^1H NMR ($CDCl_3$) δ 0.22 (9 H, s), 0.99, 1.15, 1.21, 1.23, 1.26, 1.29 (each 3 H, s), 1.61 (2 H, br s), 1.63 (2 H, br s), 1.52 (1 H, dd, J = 6, 1 Hz), 3.51 (1 H, dd, J = 11, 1 Hz), 3.99 (1 H, dd, J = 6, 11 Hz); ^{13}C NMR ($CDCl_3$) δ 0.3 (q), 16.0 (q), 23.8 (q), 25.5 (d), 26.5 (q), 27.7 (q), 27.8 (s), 28.1 (q), 28.6 (q), 36.2 (t), 39.3 (t), 41.6 (s), 44.4 (s), 45.2 (s), 56.1 (t), 196.8 (s), 198.7 (s); MS m/e 350 (M^+); HRMS calcd for $C_{19}H_{34}N_2SSi$ 350.2211, found 350.2196. **19b**: a colorless oil; ^1H NMR ($CDCl_3$) δ 0.16 (9 H, s), 1.13 (3 H, s), 1.16 (3 H, s), 1.27 (9H, s), 1.41 (9 H, s), 5.07 (1 H, d, J = 10 Hz), 5.14 (1 H, d, J = 17 Hz), 6.00 (1 H , dd, J = 10, 17 Hz); ^{13}C NMR ($CDCl_3$) δ 0.21 (q), 25.0 (q), 25.6 (q), 30.3 (q), 30.6 (q), 40.2 (s), 41.7 (s), 42.0 (s), 43.3 (s), 112.9 (t), 144.7 (d), 155.2 (s), 178.3 (s); MS m/e 352 (M^+, 2%), 337 (3), 295 (36), 223 (46), 111 (82), 73 (100), 57 (43). **20b**: colorless crystals; mp 82.5—83.5 °C; ^1H NMR ($CDCl_3$) δ 0.21 (9 H, s), 0.99 (3 H, s), 1.23 (3 H, s), 1.33 (9 H, s), 1.35 (9 H, s), 1.52 (1 H, dd, J = 1, 6 Hz), 3.51 (1 H, dd, J = 11, 1 Hz), 3.99 (1 H, dd, J = 6, 11 Hz); ^{13}C NMR ($CDCl_3$) δ 0.53 (q), 15.9 (q), 24.0 (q), 27.8 (d), 28.3 (s), 30.3 (q), 31.3 (q), 41.5 (s), 41.6 (s), 42.9 (s), 56.3 (t), 189.6 (s), 196.3 (s); MS m/e 337 (M^+-15, 13.5%), 295 (100), 73 (50), 57 (16); HRMS calcd for $C_{18}H_{33}N_2SSi$ ($C_{19}H_{36}N_2SSi$-CH_3) 337.2134, found 337.2144. **21a**: a colorless oil; ^1H NMR ($CDCl_3$) δ 0.17 (9 H, s), 1.07, 1.19, 1.20, 1.25, 1.36, 1.53 (each 3 H, s), 1.65 (4 H, s), 1.98 (1 H, d, J = 9 Hz), 3.06 (1 H, dd, J = 4, 9 Hz), 3.65 (1 H, dd, J = 4 Hz); ^{13}C NMR ($CDCl_3$) δ -1.1 (q), 23.1 (q), 25.5 (q), 26.4 (q), 27.1 (q), 27.5 (q), 28.1 (q), 37.1 (t), 39.4 (t), 43.9 (s), 44.9 (s), 46.8 (t), 51.9 (d), 54.0 (s), 59.8 (s), 180.9 (s), 184.5 (s); HRMS calcd for $C_{19}H_{34}N_2SeSi$ 398.1655, found 398.1643. **22a**: a colorless oil; ^1H NMR ($CDCl_3$) δ 0.16 (9 H, s), 1.13 (3 H, s), 1.15 (3 H, s), 1.21 (3 H, s), 1.24 (3 H x 2, s), 1.36 (3 H, s), 1.59-1.65(4 H, m), 1.90 (1 H, d, J = 7 Hz), 2.97 (1 H, d, J =10 Hz), 3.24 (1 H , dd, J = 7, 10 Hz); MS m/e 398 (M^+, 67.5%), 383 (10), 357 (12.5), 325 (22), 238 (30), 180 (86), 138 (28.5), 11 (18), 73 (100). **21b**: a colorless

oil; ^{1}H NMR ($CDCl_3$) δ 0.16 (9 H, s), 1.22 (3 H, s), 1.23 (3 H, s), 1.27 (6 H, s), 1.40 (6 H, s), 1.92 (1 H, dd, J = 1, 7 Hz), 2.95 (1 H, dd, J = 1, 10 Hz), 3.22 (1 H, dd, J = 7, 10 Hz); ^{13}C NMR ($CDCl_3$) δ 0.47 (q), 17.3 (q), 22.1 (q), 26.0 (q), 28.5 (s), 30.2 (q), 30.5 (q), 39.0 (s), 40.2 (s), 40.4 (t), 41.7 (s), 176.4 (s), 179.0 (s); MS m/e 400 (M^+, 15%), 385 (4), 343 (35), 244 (14), 180 (11), 140 (32), 73 (100), 57 (88). **21c**: a colorless oil; ^{1}H NMR ($CDCl_3$) δ -0.20 (9 H, s), 1.07 (3 H, s), 1.47 (3 H, s), 1.93 (1 H, d, J = 12 Hz), 3.02 (1 H, dd. J = 5, 12 Hz), 3.72 (1 H, d, J = 5 Hz), 7.2-7.8 (10 H, m); MS m/e 440 (M^+, 15%), 180 (100); HRMS calcd for $C_{23}H_{28}N_2SeSi$ 440.1184, found 440.1168. **21d**: a pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 1.06 (3 H, s), 1.29 (3 H, s), 1.91 (1 H, dd), 2.37 (1 H, d), 3.01 (1 H, d), 3.40 (1 H, dd), 7.1-7.7 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 23.5 (q), 23.9 (q), 27.6 (q), 35.1 (d), 42.7 (d), 127.6 (d), 128.1 (d), 128.8 (d), 129.0 (d), 129.7 (d), 130.0 (d), 135.5 (s), 137.7 (s), 162.8 (s), 176.4 (s); MS m/e 368 (M^+, 44%), 180 (100), 77 (29); HRMS calcd for $C_{20}H_{20}N_2Se$ 368.0790, found 368.0785.

Acid Catalyzed Reaction of Thiiranimine **19a**.

A drop of a CCl_4 solution of CF_3CO_2H (ca.10 μL/mL) was added to a solution of **19a** (ca. 20 mg) in 0.4 mL of CCl_4 at room temperature in an NMR tube. ^{1}H NMR spectrum of this mixture after 3 h demonstrated quantitative conversion to **11a**. A CCl_4 solution of **19a** without acid did not change after 3 h at room temperature.

Acid Catalyzed Reaction of Thiiranimine **19b**.

A drop of a CCl_4 solution of CF_3CO_2H (ca.10 μL/mL) was added to a solution of **19b** (ca. 20 mg) in 0.4 mL of CCl_4 at room temperature in an NMR tube. ^{1}H NMR spectrum of this mixture after 10 min demonstrated major conversion to **11b** and trace amount of **20b**. When a $CDCl_3$ (0.4 mL) solution of **19b** (ca. 20 mg) in an NMR tube was heated at 60 °C for 1.5 h, the ^{1}H NMR spectrum demonstrated quantitative conversion to **11b**.

Crystal Data and Structural Analysis of **11a**.

An orange crystal of dimensions 0.6 x 0.6 x 0.5 mm for **11a**, obtained by recrystallization from a hexane-dichloromethane solution at 25 °C, was used for X-ray analysis. Diffraction measurements were made on a RIGAKU-AFC-4 computer controlled Kappa axis diffractometer by using graphite-monochromatized Mo Kα radiation. Crystal data and data collection parameters and results of the analyses are listed in Table 3. Calculations were performed with UNICS III programs[17] for full-matrix least-squares refinement. The ω-2θ scan technique was adopted by varying the ω scan width as a function of θ (ω scan width = 0.7 + 0.350 tan θ). Final residuals of R = 0.054 and R_w = 0.062 were obtained, where $w = 1 / (0.0019|Fo|^2 - 0.024|Fo| + 0.612)$.

Table 3. Crystal and Experimental Data of **11a**.

Formula:	$Si_1S_1C_{19}H_{34}N_2$
Formula weight =	340
Crystal system :	Monoclinic
Space group:	$P2_1/n$ Z=4
Lattice const.	a = 12.640(2) Å
	b = 20.526(2) β = 99.31(3)
	c = 8.463(1)
Cell volume	V = 2166.9(5) $Å^3$
Density (cal)	1.05 g/cm^3
R	0.054
R_w	0.062
	$W = 1 / (0.0019 \|Fo\|^2 - 0.024 \|Fo\| + 0.612)$
No. of reflections used =	3559
Crystal size	0.6 x 0.6 x 0.5 mm
μ	1.09 cm^{-1}
Measurement :	RIGAKU-AFC-4
	graphite-monochlomated Mo K_α
Program system :	UNICSIII
Structure determination :	MULTAN 78
Refinement :	Full Matrix least-squares
	24H atoms found in D-fourier method
	10H atoms located by calculation

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