Tetrahedron Letters, Vol.31, No.25, pp 3571-3574, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

NOVEL RING TRANSFORMATION IN THE REACTIONS OF 2-ALKYLIDENE-1,3,4-THIADIAZOLINES AND THEIR SELENIUM ANALOGUES

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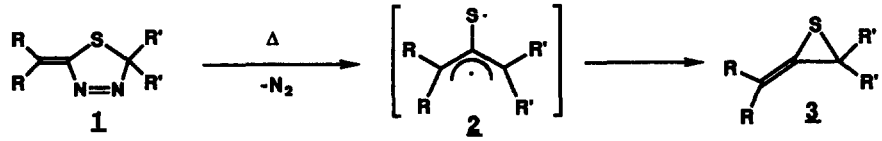
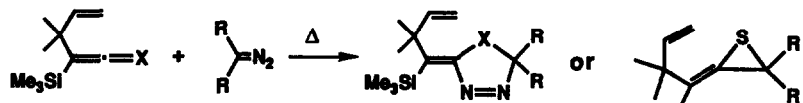
Summary: Several new reaction modes were found in the thermolysis and photolysis of allyl substituted 2-alkylidene-1,3,4-thiadiazolines and their selenium analogues. Photochemical reaction of 2-alkylidene-1,3,4-thiadiazolines resulted in a novel formation of thiiranimine derivatives via azathioallyl intermediates.

The chemistry of 1,3,4-chalchogenadiazolines have been extensively explored as a means of providing synthetic routes to a variety of hindered olefins[1] and also as for generating thio- and selenocarbonyl ylides.[2] However, only a few has been reported on the thermolysis of 2-alkylidene-1,3,4-thiadiazolines **1**.[3] Thermal decomposition of **1** may be one of a good approach to produce allene episulfide **2**. We have already reported that the thermal decomposition of 2-alkylidene-1,3,4-thiadiazoline derivatives **1** produced allene episulfides **3** via thioallyl intermediate **2**.[3b,c] We now describe novel ring transformation reactions in the thermolysis and photolysis of allyl substituted 2-alkylidene-1,3,4- thiadiazolines and their selenium analogues.



1 **2** **3**

2-Alkylidene-1,3,4-thiadiazolines **6** and their selenium analogues **7** were synthesized by cycloaddition of diazo compounds with thioketene **4**[6a] or selenoketene **5**[6b] in good yields. (Table 1)[4]



4 X = S
5 X = Se

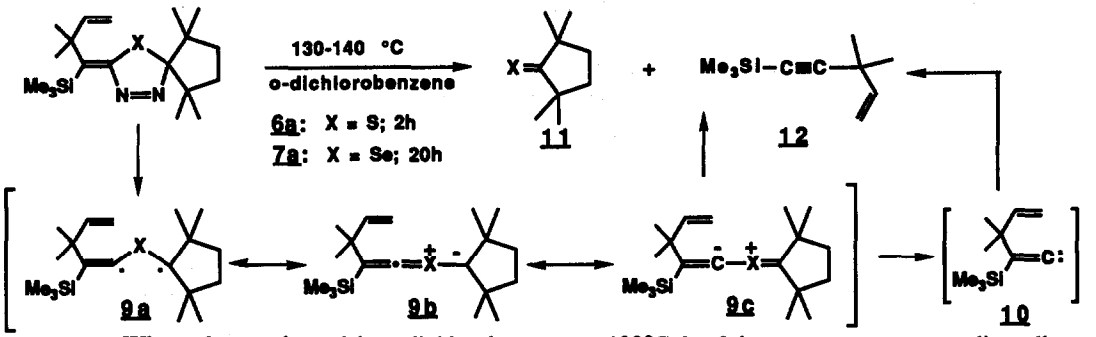
6
7

8 **

Table 1 Synthesis of 2-alkylidene-1,3,4-thiadiazolines and their selenium analogues

X	R, R	reaction conditions	products	isolated yields
S		benzene/reflux/9h	(6a)	44% [5]
	^{t}Bu x 2	benzene/reflux/13h	(6b)	79%
	Ph x 2	$ClCH_2CH_2Cl$/80°C/15h	(8)	30%**
Se		Et_2O/reflux/12h	(7a)	56%
	^{t}Bu x 2	Et_2O/reflux/12h	(7b)	60%
	Ph x 2	Et_2O/r.t./3days	(7c)	36%

Scheme 1

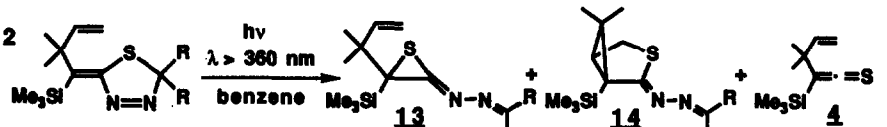


When **6a** was heated in o-dichlorobenzene at 130°C for 2 hours, not a corresponding allene episulfide **8a** but a thioketone **11** (X=S) was obtained along with a silylacetylene **12** quantitatively. (Scheme 1) The thermolysis of the selenium analogue **7a** was also examined to give selenoketone **11** (X=Se) and **12**.

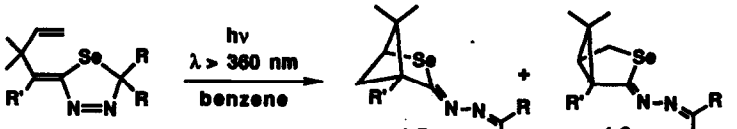
A plausible mechanism is shown in Scheme 1. The initial intermediate **9a**, generated by thermal denitrogenation of **6a** or **7a** should resonate to the ylides **9b** and **9c**. The silylacetylene **12** might be produced by the carbon-chalcogen bond cleavage of **9c** leading to a formation of **11** (X=S or Se) and the alkylidenecarbene **10** followed by the ready migration of trimethylsilyl group.[7] The selective carbon-chalcogen bond cleavage and the lack of ring closure product **8a** or its selenium analogue, which is in a sharp contrast to the facile allene episulfide formation from **1** via **2**, are probably due to the steric hindrance of the bulky substituents in these systems.[8]

Meanwhile, a quite different reaction mode was found in the photolysis of **6** and **7**.(Scheme 2) An irradiation of benzene solution of **6a** with a medium pressure mercury lamp through a phenanthlene filter solution at room temperature for 10 minutes gave thiiranimine derivative **13**[9] in 51 % yield along with 15 % of bicyclo [3.1.0] thiahexane derivative **14**.[10] Compound **6b** gave thioketene **4** together with **13b** and **14b**. The photochemical reactions of **7a-d** are more complicated, however, bicyclic compounds **15**[11] and/or **16**[12] were obtained in low yields after an exhaustive chromatographic separation.

Scheme 2



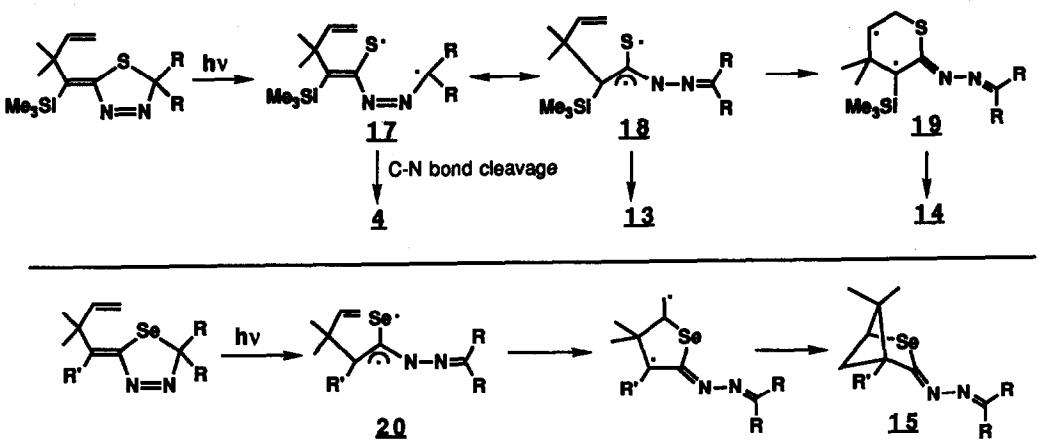
6a: R, R =	(λ_{max} = 348 nm)	51%	15%	--
6b: R = R = ^{t}Bu	(λ_{max} = 355 nm)	19%	29%	11%



7a - 7c: R' = SiMe$_3$, 7d: R' = H

7a: R, R =	(λ_{max} = 362 nm)	8%	4%
7b: R = R = ^{t}Bu	(λ_{max} = 375 nm)	5%	--
7c: R = R = Ph	(λ_{max} = 373 nm)	14%	--
7d: R = R = Ph	(λ_{max} = 348nm)	8%	--

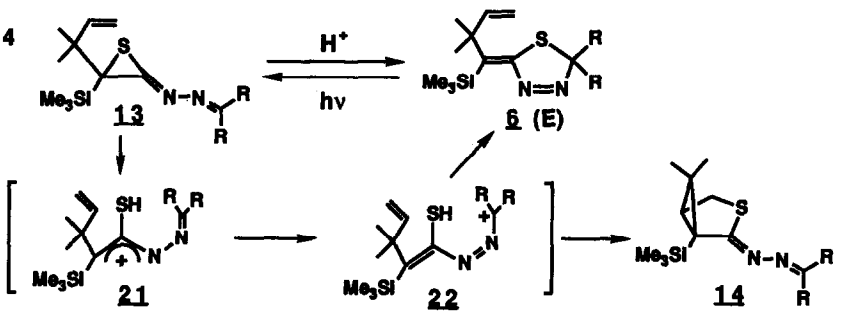
Scheme 3



The conceivable mechanism is illustrated in Scheme 3. At first the biradical intermediate **17** might be generated by the clavage of C-S bond of **6**, opposite to the exocyclic double bond, followed by three competitive routes : (1) C-N bond fission to yield **4**, (2) new C-S bond formation to afford **13** via azathioallyl intermediate **18**, (3) formation of bicyclic compound **14** by the intramolecular cyclization of **19**. The competitive formation of **15** with **16** in the case of **7** is also rationalized by the intramolecular trapping of the alternative biradical intermediate **20**. It is noteworthy that the reaction mode of the 2-alkylidene-1,3,4-chalchogenadiazolines thus described is considerably different from that of the concerted cheletropic reaction in case of simple 1,3,4-thiadiazolines .[2a]

In addition, thiiranimines **13** here obtained were found to undergo a quantitative isomerization into **6** by the addition of catalytic amount of trifluoroacetic acid. This interesting acid catalysed ring transformation can be interpreted as the intramolecular reaction via the azathioallyl cation **21**. The predominant formation of **6** over **14** is well explained by the preferential nucleophilic attack of sulfur atom toward the stabilized cationic reaction center by the two alkyl groups in the resonance structure **22**.

Scheme 4



R,R	solv.	reaction conditions	acid	products 6	products 14
	CCl_4	r.t. / 3 h	CF_3CO_2H	quant.	----
	CCl_4	r.t. / 3 h	none	no reaction	
^{t}Bux2	C_6D_6	r.t. / 10 min.	CF_3CO_2H	main.	trace

References and Notes

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3. (a) Middleton, W. J., *J. Org. Chem.*, **34**, 3201 (1969). (b) Furuhata T. and Ando W., *Tetrehedron Lett.*, **28**, 1179 (1987). (c) Tokitoh, N.; Choi, N. and Ando, W., *Chem. Lett.*, 2177 (1987).
4. All the products described here gave satisfactory spectral data, and the data of **6a** are shown as the representative as follows: **6a**; pale yellow crystals, mp. 67.5-68 °C; ^{1}H-NMR($CDCl_3$) δ 0.30 (9H,s), 0.67 (6H,s), 1.13 (6H,s), 1.42 (6H,s), 1.68 (2H,dd, J=13, 6 Hz), 2.21 (2H, dd, J=10.5 Hz), 6.06 (1H, 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); MS, m/z 350(M^+); UV (cyclohexane) λmax 348(log e = 3.82) ; Elemental Anal. Found C; 64.75, H; 9.76, N; 7.85 %, calcd for $C_{19}H_{34}N_2SSi$ C; 65.08, H; 9.77, N; 7.99 %.
5. **6a** was found to be yielded mainly as E form (40 %) together with meiner Z form (4 %).These configurations were determined by ^{1}H, ^{13}C-NMR and X-ray structure analysis.
6. (a) Schaumann, E. and Grabley, F. F., *Tetrahedron Lett.*, **18**, 4307 (1977). (b) Schaumann, E. and Grabley, F. F., *ibid.*, **21**, 4251 (1980).
7. (a) Sekiguchi A. and Ando, W., *Organometallics*, **6**, 1857 (1987). (b)The migration of trimethylsilyl group has been postulated in the reaction of germathiocarbonyl ylide. Tsumuraya, T. ; Ando, W. and Goto, M., *Tetrahedron Lett.* , **27**, 5105 (1986). Ando, W. and Tsumuraya, T., *Organometallics*, **8**, 1467 (1989).
8. An analogous carbene formation has been already described in the thermolysis of 1,3,4-oxadiazoline derivatives, though the reaction mechanism was interpreted as a favorable carbonyl compound formation. see (a) Shimizu N. and Bartlett P. D., *J. Am. Chem. Soc.*, **100**, 4260 (1978). (b) Prakash, G. K. S.; Ellis R. W.; Felberg J. D. and Olah G. A., *ibid*, **108**, 1341 (1986). (c) Feller D.; Davidson E. R. and Borden W. T., *ibid*, **106**, 2513 (1984). and ref. 3(b).
9. **13**; colorless oil, ^{1}H-NMR ($CDCl_3$) δ 0.17 (9H,s), 1.13, 1.16, 1.17, 1.20, 1.32, 1.34 (each 3H, s), 1.64 (4H ,s), 5.07 (1H,d,J=14 Hz), 5.15 (1H,d,J=17 Hz), 6.00 (1H,dd,J=14,17 Hz); 13C-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/z 350(M^+), Exact Mass; m/z 350.2194 calcd for $C_{19}H_{34}N_2SSi$ 350.2211.
10. **14**; white crystals, mp. 114-114.5 °C ; ^{1}H-NMR ($CDCl_3$) δ 0.22 (9H,s), 0.99, 1.15, 1.21, 1.23, 1.26, 1.29 (each 3H,s), 1.61 (2H,dd),1.63 (2H,dd), 1.52 (1H,dd,J=6,1Hz), 3.51 (1H,dd,J=11,1Hz), 3.99 (1H,dd,J=6,11Hz); ^{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/z 350(M^+); Exact Mass; m/z 350.2196 calcd for $C_{19}H_{34}N_2SSi$ 350.2211.
11. **15**; ^{1}H-NMR ($CDCl_3$) δ 0.17 (9H,s), 1.17, 1.19, 1.20, 1.25, 1.36, 1.53 (each 3H,s),1.64-1.66 (4H,m), 1.98(1H,d,J=9Hz),3.06(1H,dd,J=4,9Hz),3.65(1H,d,J=4Hz).
12. **16**; ^{1}H-NMR ($CDCl_3$) δ 0.16 (9H,s),1.13 (3H,s),1.15 (3H,s), 1.21 (3H,s),1.24 (3Hx2,s),1.36 (3H,s), 1.59-1.65(4H,m), 1.90 (1H,d,J=7Hz), 2.97 (1H,d,J=10Hz), 3.24 (1H,dd,J=7,10Hz).

(Received in Japan 18 April 1990)