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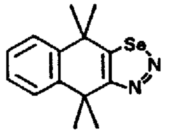
Competitive Photochemical Decarcogenation of 1,2,5-Thiadiselenole

Norihiro Tokitoh, Hitoshi Ishizuka, Akira Yabe,[†] and Wataru Ando*
Department of Chemistry, University of Tsukuba,
1-1-1 Tennohdai, Tsukuba, Ibaraki 305, Japan
[†]National Chemical Laboratory for Industry,
1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Summary: Monitoring of the photolysis of 1,2,5-thiadiselenole(**4**) in low temperature matrix by electronic spectroscopy has implied an initial formation of a novel spirothiaselenirane intermediate, which is consistent with the competitive photochemical decarcogenation of **4** in solution.

Although the diversity and biological activity of polysulfides has attracted much attention[1] and their characteristic sulfide exchange associated with sulfur-sulfur bond cleavage has been extensively studied,[2] the chemistry of their selenium analogues has not been fully investigated on account of the scarcity of suitable synthetic method.[3] Recently, we have succeeded in a facile synthesis of stable 1,2,3-trithiole (2) and 1,2,3-triselenole (3) by the thermal reactions of sterically protected 1,2,3-selenadiazole (1) with elemental sulfur and selenium.[4] Further thermal sulfurization of (3) was also examined to give a novel 1,2,5-thiadiselenole ring system (**4**).[4]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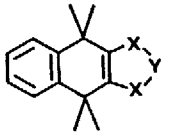
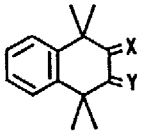
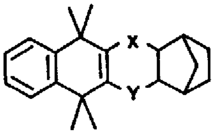
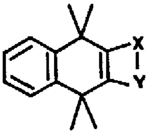

2 (X=Y=S)
3 (X=Y=Se)
4 (X=Se,Y=S)


5 (X=Y=S)
6 (X=Y=Se)
11 (X=Se,Y=S)


7 (X=Y=Se)
8 (X=Se,Y=S)


10 (X=Se,Y=S)
13 (X=Y=Se)
19 (X=Y=S)

We present here a new aspect in the photolysis of **4** implying the initial formation of a spirothiadiselenirane intermediate before decarcogenation. As previously described 2 and 3 were photochemically decarcogenated to generate intermediary 1,2-dithione (5) and 1,2-diselone (6), which effectively underwent cycloaddition with norbornene.[4] Meanwhile, the photolysis($h\nu$, $\lambda > 300$ nm) of **4**(1 mmol) in 2 ml of chloroform in the presence of norbornene(5 mmol) at 15 °C resulted in an unexpected formation of two kinds of cycloadducts (**7**, 9%) and (**8**, 5%), suggesting a competitive formation of 1,2-selenoxothione and 1,2-diselone intermediates (**11** and **6**).

To elucidate the mechanism of this unusual photochemical decarcogenation, the photolysis of **4** with light of λ=254 nm was performed in argon matrix at 20 K and monitored by electronic spectroscopy[5] to show two characteristic absorption maxima at 395 and 540 nm (**Figure 1a**). On the other hand, 1,3-thiaselenole-2-one (**9**) was photodecarbonylated under similar conditions with an appearance of shoulder peaks at 420 and 620 nm in the electronic spectra (**Figure 1b**), which are attributable to the 1,2-thiaselenete and 1,2-selenoxothione intermediates (**10** and **11**).[6]

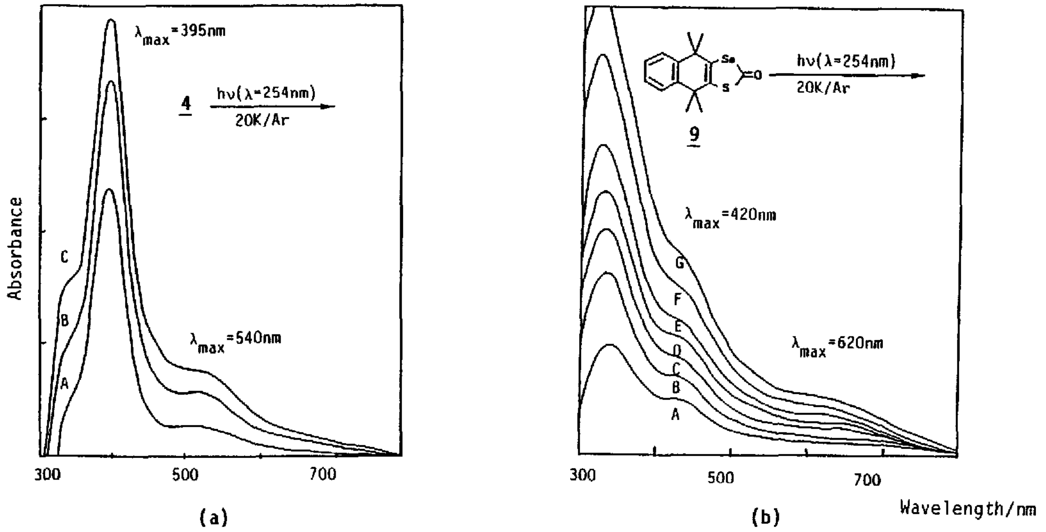
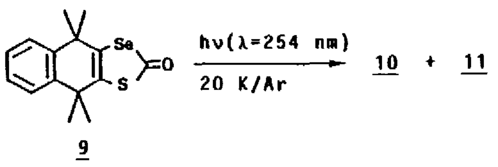
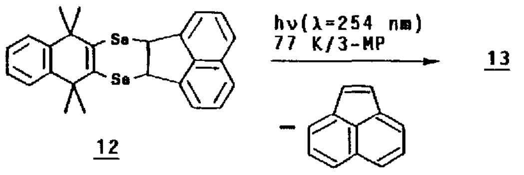


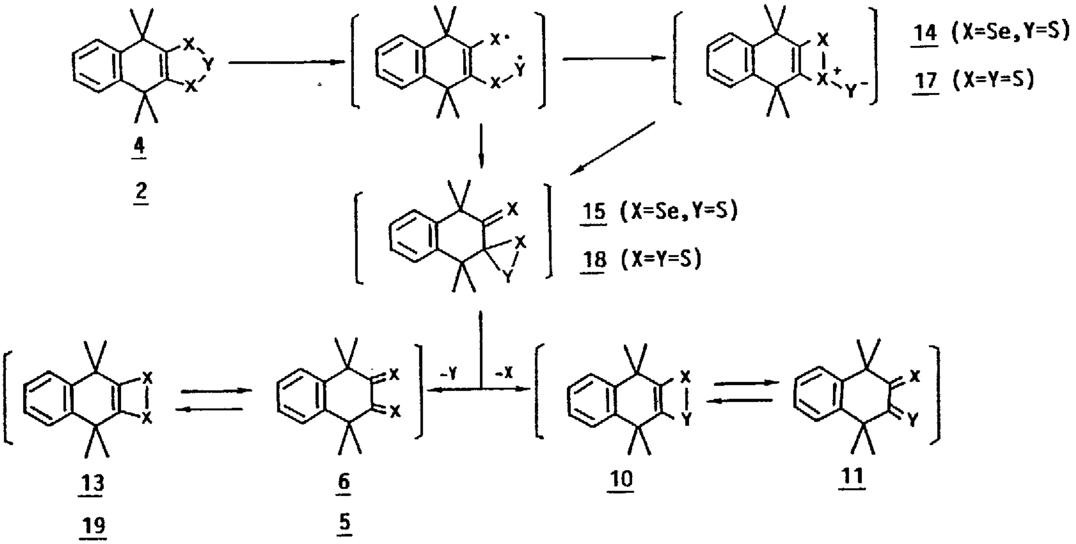
Figure 1. (a) Photolysis of **4** in Ar Matrix at 20 K; Difference Electronic Spectra after Irradiation with Light of λ=254 nm (A; 2 min, B; 5 min, C; 18 min) and **(b)** Photolysis of **12** in Ar Matrix at 20 K; Difference Electronic Spectra after Irradiation with Light of λ=254 nm (A; 3 min, B; 8 min, C; 18 min, D; 28 min, E; 38 min, F; 48 min, G; 70 min).

Furthermore, when photochemical retrocycloaddition of 1,4-diselenin derivative (**12**) was carried out with light of λ=254 nm in 3-methylpentane glass matrix at 77 K, only a broad absorption maxima at 465 nm, which is assignable to 1,2-diselenete intermediate (**13**), was observed.

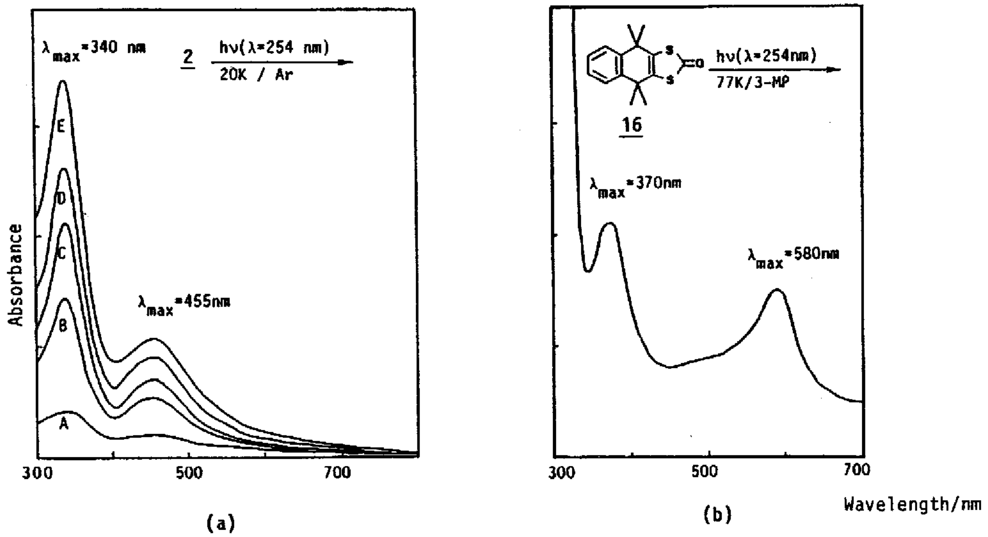




The disagreement of the electronic spectra obtained by the photolysis of **4**, **9**, and **12** in low temperature matrices and the comparison of the wavelength values of each absorption maxima with those of known organosulfur and organoselenium compounds suggest that the two absorption maxima observed at 395 and 540 nm in the case of **4** might be attributable to the initial intermediates such as thioselenoxide (**14**) and spirothiaselenirane (**15**), respectively. The competitive photochemical decarcogenation of **4** is consistently rationalized by assuming the intermediacy of **15** and its instability leading to a facile extrusion of a carcogen atom as shown in the following scheme.



The photolysis of 2 was examined in argon matrix at 20 K to show two absorption maxima at 340 and 455 nm (**Figure 2a**), however, the photodecarbonylation of 1,3-dithiole-2-one (**16**) under similar conditions gave quite a different spectra having two absorption maxima at 370 and 580 nm (**Figure 2b**), which correspond to 1,2-dithiete and 1,2-dithione intermediates (**19** and **5**).



(a)

(b)

Figure 2. **(a)** Photolysis of **2** in Ar Matrix at 20 K; Difference Electronic Spectra after Irradiation with Light of λ=254 nm (A; 0.5 min, B; 1.5 min, C; 2.5 min, D; 3.5 min, E; 7.5 min) and **(b)** Photolysis of **16** in 3-Methylpentane at 77 K; Difference Electronic Spectrum after Irradiation with Light of λ=254 nm for 2 min.

These results are also interpreted with the initial formation of thiosulfoxide (**17**) and spirodithiirane (**18**) in advance of the decarcogenative formation of 1,2-dithiete and 1,2-dithione intermediates.

In view of a wide chemistry of 1,2-dithiones and their valence isomeric 1,2-dithietes[7] and a recent progress in the field of their selenium analogues,[8] the novel decarcogenation reaction in the photolysis of cyclic polysulfides and polyselenides thus described is of great interest as a new route towards such organosulfur and organoselenium reactive species.

References and Notes

1. See, for example; I. W. J. Still and G. W. Kutney, Tetrahedron Lett., **21**, 1939 (1981); K. Morita and S. Kobayashi, Chem. Pharm. Bull., **15**, 988 (1967); Tetrahedron Lett., **1966**, 573; S. J. Wratten and D. J. Faulkner, J. Org. Chem., **41**, 2465 (1976) and references cited in these reports.
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5. The cryostat system used for the argon matrix experiment is the same one reported by Chapman et al.[9] For electronic spectra measurement, the substrate and argon gas were deposited on the sapphire plate cooled to 20 K by Air Products Displex refrigerator. The spectra were recorded through the quartz windows on a Shimadzu UV-265 spectrometer.
6. The assignment of **10** and **11** was confirmed with the initial appearance of an absorption maximum at 424 nm by the irradiation of **9** with light of λ=254 nm in 3-methylpentane glass matrix at 77 K followed by the isosbestic increase of an absorption maximum at 615 nm after the second irradiation with light of $300 < \lambda < 550$ nm.
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