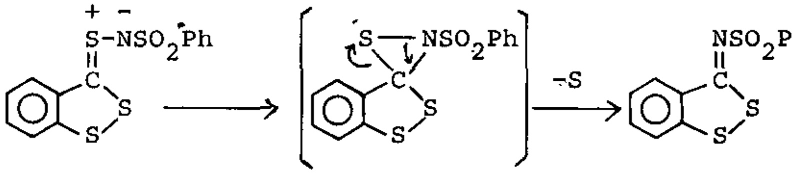
# DERIVATIVES OF 1,2-DITHIOLE-3-THIONES.III.[1] A NOVEL DESULFURIZATION OF 4,5-BENZO-1,2-DITHIOLE-3-THIONE IMIDE OR ITS SELENIUM ANALOGUE

Seizo Tamagaki, Keishi Sakaki, and Shigeru Oae*

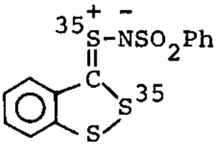
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558, Japan

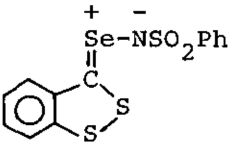
N-Benzenesulfonylimide of 4,5-benzo-1,2-dithiole-3-thione(C=$^{35}$S) was thermally desulfurized to afford a corresponding 3-(N-benzenesulfonyl)imine with predominant extrusion of the exocyclic thiono sulfur atom, while with its selenium analogues, the exclusive loss of thiolo sulfur instead of exocyclic selenium atom was observed, resulting in the formation of the selenium-migrating product, i.e., 4,5-benzo-1,2-thiaselenole-3-(N-benzenesulfonyl)imine.

Recently we have reported that 4,5-benzo-1,2-dithiole-3-thione N-benzenesulfonylimide[2] was thermally desulfurized, eventually giving a rearranged product, i.e., 4,5-benzo-1,2-dithiole-3-(N-benzenesulfonyl)imine. In view of the kinetic data, the reaction is presumed to proceed through the initial formation of a thiaziridine ring followed by the fast expulsion of sulfur, apparently relieving inherent strain of the three-membered ring (Scheme 1).[3]


(Scheme 1)

In order to understand the mechanism of the desulfurization we have synthesized $^{35}$S-labeled imide(Ia) and its selenium analogue(Ib) (Anal: Calcd. for $C_{13}H_9NO_2S_3Se$: C, 40.41; H,2.33; N,3.68%. Found: C,40.13; H,2.18; N,3.44%, mp 146-146.5°) and subjected them to the usual thermolysis. We have obtained an interesting result and hence wish to report here the implication of the results on the mechanism of sulfur extrusion.


(Ia)


(Ib)

First when the imide(Ib) of 4,5-benzo-3-selenoxo-1,2-dithiole(Anal: Calcd. for $C_7H_4S_2Se$: C,36.36; H,1.73%. Found: C,36.13; H,1.69%, mp 83-84°) which was prepared in a moderate yield by the reaction of 4,5-benzo-3-methylthio-1,2-dithiolium iodide with NaHSe,[4] was thermolyzed by either refluxing in $CH_3CN$ or heating without solvent at its decomposition temperature, an isolated product was not the expected compound (IIa), but an unexpected unknown compound, i.e., 4,5-benzo-1,2-thiaselenole-3-(N-benzenesulfonyl)imine(IIb) (Anal: Calcd. for $C_{13}H_9O_2NS_2Se$: C,44.06; H,2.54; N,3.95%. Found: C,43.86; H,2.54; N,3.83%, mp 141-142°). However, the expected product (IIa) was detected in a negligible yield of 4% when the reaction was carried out at a somewhat elevated temperature.

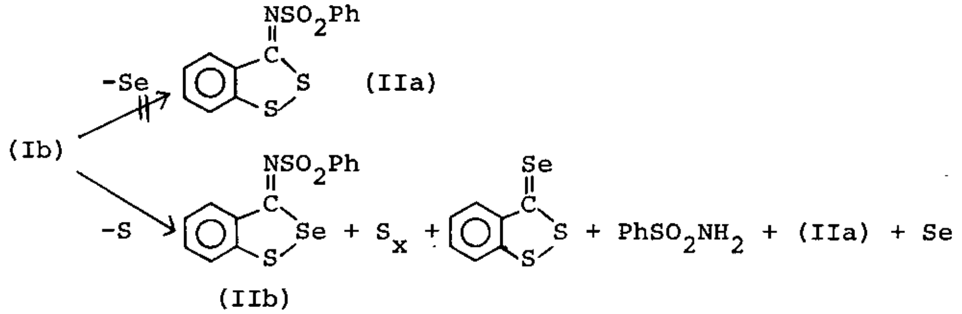
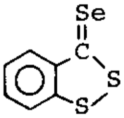
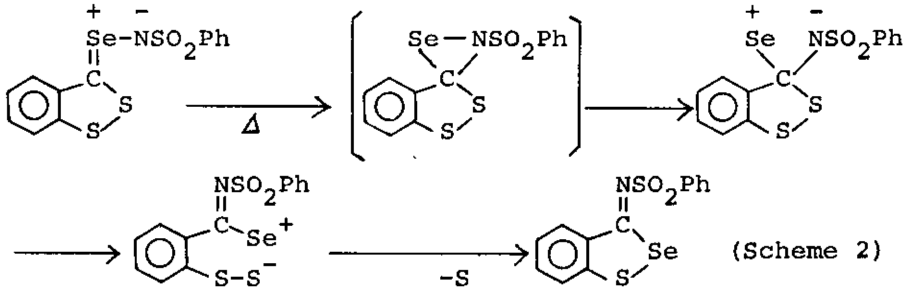


Table 1. Thermal Decomposition of Ib. (yield%)

| reaction condition | (IIb) | $S_x$ |  | $PhSO_2NH_2$ | (IIa) | Se |
|---|---|---|---|---|---|---|
| refl. in $CH_3CN$ | 48.7 | 45.1 | 29.9 | 48.3 | trace | trace |
| decompn. temp. | 62.2 | 50.2 | 10.3 | 7.4 | 3.8 | trace |

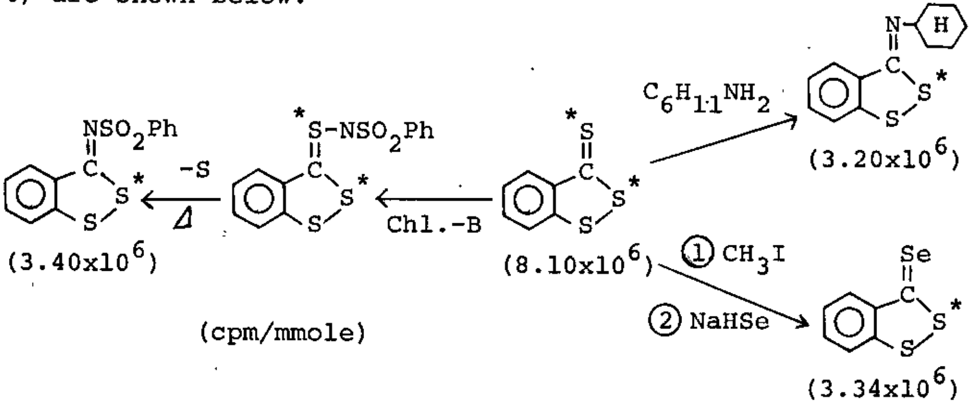
In addition, the reduced 4,5-benzo-3-selenoxo-1,2-dithiole and an equimolar amount of the sulfonamide were isolated as the by-products. The occurrence of the exclusive extrusion of sulfur atom rather than that of selenium atom indicates undoubtedly that the loss of the sulfur atom should have taken place _via_ the scission of the dithiole ring itself. The probable reaction scheme may be outlined as follows:

(Scheme 2)



To our knowledge this is the first reported example of the predominant expulsion of the ring sulfur in 1,2-dithiole-3-thione system.[5]

Moreover, the mechanism of this type of sulfur atom extrusion found in the reaction of the selenium system can no longer be applicable to the sulfur analogue. Then the imide (Ia), unequally labeled with $^{35}S$ both at the thiono sulfur and the S-2 dithiolo sulfur with the ratio of 60.5% and 39.5%, respectively, was prepared and subjected it to the usual thermolysis at its decomposition temperature. The $^{35}S$ counting and the calculated values thus obtained (experimental error 5%) are shown below:



In the case of the sulfur analogue the mechanism of desulfurization seems to be entirely different; namely, the thiono sulfur is predominantly kicked out (92±5%) in the reaction with the corresponding sulfur analogue with a small extent of the concomitant extrusion of sulfur atom in the dithiole ring (8±5%) (Scheme 1).

The reason for the strikingly different behavior in the reactions between the sulfur and the selenium analogues still remains obscure; however, the behavior could be explained by the difference in the instability between the intermediary thia- and selenaziridine rings.[6]

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