DERIVATIVES OF 1,2-DITHIOLE-3-THIONES.IV.
OXIDATION OF 4,5-BENZO-3-SELENOXO-1,2-DITHIOLE

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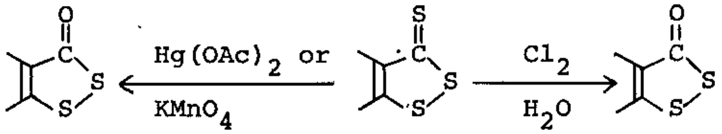
The desulfurizative oxidation of 1,2-dithiole-3-thiones with various oxidizing reagents was reexamined using 4,5-benzo-3-selenoxo-1,2-dithiole as a typical substrate. The product thus obtained was 4,5-benzo-1,2-thiaselenole-3-one, but not an expected 4,5-benzo-1,2-dithiole-3-one. The reaction pathway *via* a selenine[1] is postulated.

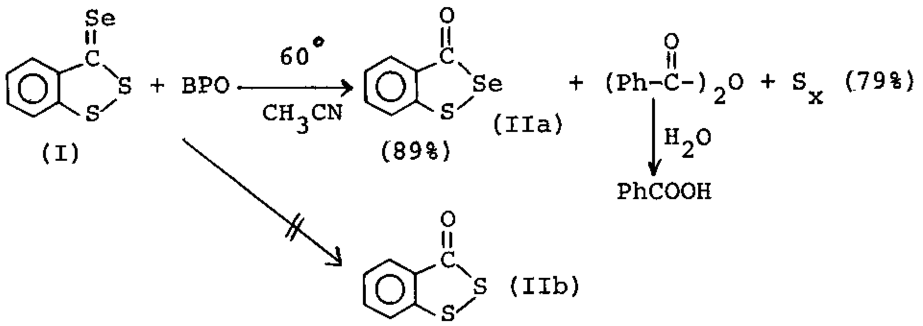
During the course of the studies on the thermolysis of 3-selenocarbonyl imides of 3-selenoxo-1,2-dithiole, we have found that the original exo selenium atom was eventually incorporated into the final ring, imine-product, while one of the sulfur atoms in the dithiole ring was eliminated as elemental sulfur. We have now found that in the oxidation of 4,5-benzo-3-selenoxo-1,2-dithiole(I) with various oxidizing reagents a closely similar pattern of desulfurization takes place predominantly.

It has been well known that 4- or 5-substituted 1,2-dithiole-3-thione can be readily converted to the corresponding carbonyl compounds by treating it with aqueous $KMnO_4$[2] or mercuric acetate[3] or by chlorination followed by hydrolysis.[4]



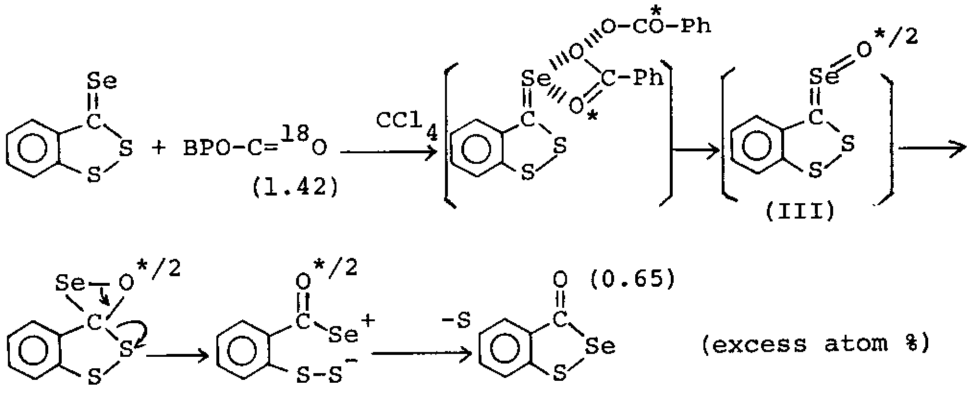
However, virtually no attention has been paid on the details of these oxidative desulfurizations of thiocarbonyl moiety of the 1,2-dithiole-3-thione system.

We now report here our results concerning the oxidative desulfurization of 4,5-benzo-3-selenoxo-1,2-dithiole. In a first attempt to obtain some critical informations on the possible migration of the selenium and the sulfur atoms, we have synthesized 4,5-benzo-3-selenoxo-1,2-dithiole(I) (Anal: Calcd. for $C_7H_4S_2Se$: C,36.36; H,1.73%. Found: C,36.13; H,1.69 %, mp 83-84°) by the reaction between 4,5-benzo-3-methylthio-1,2-dithiolium iodide and sodium hydrogen selenide[5] in H_2O-benzene and carried out the oxidation with benzoyl peroxide as a choice of oxidizing reagent. When a mixture of the selenoketone and 1.2 mole equiv of BPO-C=^{18}O was heated at 60° in CCl_4, yellow-colored elemental sulfur (0.8 equiv to the selenoketone) separated out. After the solvent was evaporated, preparative thin-layer chromatographic separation of the resulting oily residue using benzene afforded the following products (yield %).



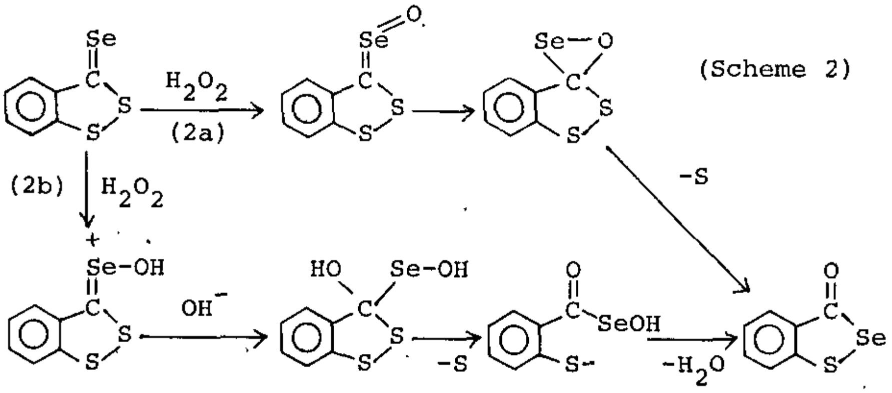
It was surprising to find that the oxidation also gave 4,5-benzo-1,2-thiaselenole-3-one(IIa)[6] instead of the anticipated corresponding sulfur analogue(IIb).

Thus the oxidation reaction resembles closely to the thermal rearrangement of 3-selenoxo imide reported in the previous paper. The mechanistic pathway, in accord with this result and the result of the ^{18}O-labeling experiments (shown below), may involve the formation of an intermediate selenine(III),[1] followed by ring closure, subsequent reopening, and desulfurization, to eventually afford the 1,2-thiaselenole-3-one(IIa) (Scheme 1).



(Scheme 1)

In a continuation of our interest in the oxidative desulfurization of this kind, the reaction with other oxidants have also been examined. All of the oxidants, which have been reported to convert the 1,2-dithiole-3-thione into the corresponding carbonyl compounds, were found to react in a similar fashion and no corresponding sulfur analogue, i.e., 1,2-dithiole-3-one(IIb), was detected in the TLC analysis except for the case with metallic oxidants (Table 1). At this stage it is still premature to suggest a most plausible mechanism. However, based on the finding that the oxidation even with ozone in dry benzene could yield the same product, a tentative mechanism one might propose is the following reaction sequence involving the selenine intermediate (Scheme 2a) rather than that via another pathway including the nucleophilic attack of hydroxide ion on the carbon-3 of the ring (Scheme 2b, taking H_2O_2 as an example).



(Scheme 2)

Thus it appears that the formation of 1,2-thiaselenole-3-one is essential to the oxidation of 3-selenoxo-1,2-dithiole systems.

Table 1. Oxidation of 4,5-benzo-3-selenoxo-1,2-dithiole(I) with various oxidants a)

oxidant	oxidant/(I)	solv.	reaction temp.	yield(%)	yield(%) b)
BPO	1.2	CH_3CN	60°	71.1	0
BPO	1.2	CCl_4	60°	57.7	0
H_2O_2	excess	C_6H_6	room	17.2	0
NaOCl	excess	C_6H_6	room	35	0
O_3	excess	C_6H_6	room	19.8	0
$Pb(OAc)_4$	1.5	AcOH	room	86.7	3.9
$Hg(OAc)_2$	2.0	AcOH	room	69.8	1.2
$KMnO_4$	excess	AcOH	room	7.0	0.3

a) no attempt has been made to optimize the reaction condition.

b) 4,5-benzo-1,2-dithiole-3-thione.

REFERENCES

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6. (IIa): IR(KBr) 1640cm^{-1}(C=O); Mass m/e 216, 188, 163.6 (metastable peak), 136; Anal: Calcd. for C_7H_4OSSe: C, C,39.07; H,1.86%. Found: C,39.45; H,1.87%; mp 79-80°.

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