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REACTION OF SELENOCARBONYL IMIDE WITH AMINES AND MERCAPTANS.[1)]

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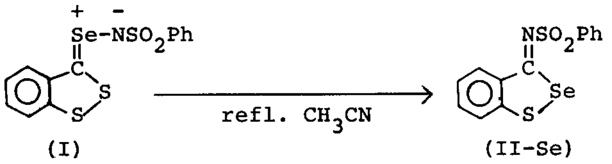
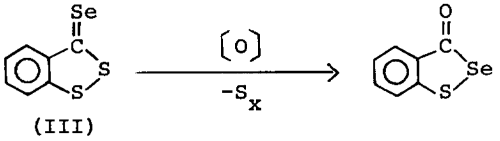
In the previous paper of this series we reported that selenocarbonyl-N-benzenesulfonylimide (I)[2)] prepared from 4,5-benzo-3-selenoxo-1,2-dithiole readily undergoes thermal desulfurizative rearrangement to afford eventually the corresponding selenium-migrated N-benzenesulfonylimine (II-Se) with extrusion of sulfur atom originally present at 2-thiolo position.[3)]



Like the thermal desulfurizative rearrangement, the migration of selenium atom was found to occur even in the oxidation of 3-selenocarbonyl-1,2-dithiole (III) with various oxidizing reagents such as hydrogen peroxide, sodium hypochlorite, ozone, and metallic acetate.[4)]

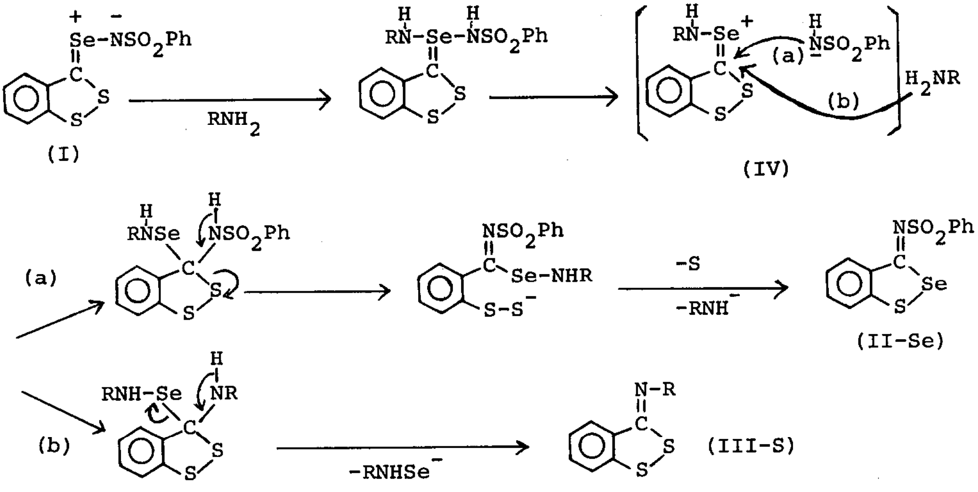


We now wish to report a similar prominent desulfurizative selenium migration in the reaction of the imide (I) with amines and mercaptans to give the product (II-Se) which was obtained only as a by-product.

We have first treated (I) with an equimolar amount of primary amine such as p-chloroaniline or t-butylamine in CH_3CN at room temperature. After 30 minutes the solvent was evaporated and a minimum amount of chloroform required to dissolve the residue was added and then the resultant solution was chromatographed on preparative TLC using benzene.

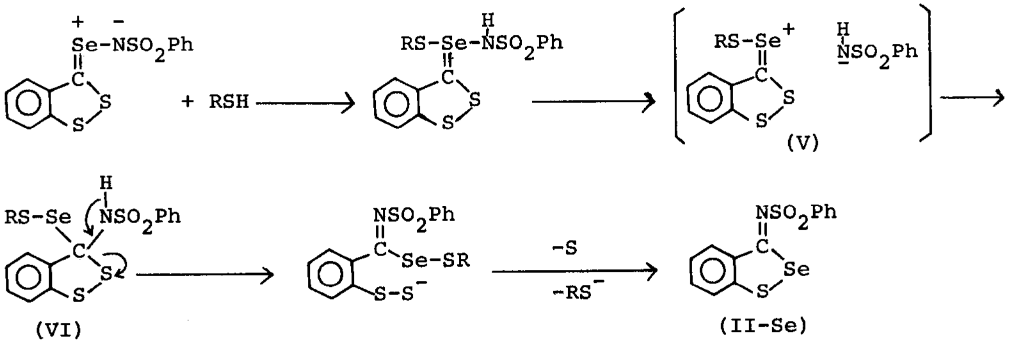
The products and yields thus obtained are summarized in Table I along with those of the reactions with mercaptans to be mentioned later. The main product thus isolated was N-aryl or alkyl substituted 4,5-benzo-1,2-dithiole-3-imine (III-S), which were identified by the comparison of their ir and uv spectra with those of the authentic samples prepared by the reaction of 4,5-benzo-1,2-dithiole-3-thione or the corresponding 3-methylthio-1,2-dithiolium iodide with the corresponding amines,5) while the minor product was assigned as the selenium migrated product, N-benzenesulfonyl-4,5-benzo-1,2-thiaselenole-3-imine (II-Se), whose structure has been elucidated already in our previous work.3) In addition, it was confirmed that under those conditions there was essentially no direct thermal conversion of I to II-Se.

Based on these products analyses, we may thus propose the following reaction mechamism involving the initial nucleophilic addition on the tetravalent selenium atom to form the intimate ion pair (IV) and the subsequent nucleophilic attack by either sulfonamide anion (path a) or aniline (path b) at carbon-3 to give the final products. The path (a) involve the nucleophilic attack by sulfonamide anion at carbon-3, and then the succeeding C-S bond rupture and desulfurization result in the formation of the new thiaselenole ring, while the path (b) involves the attack by an aniline molecule at carbon-3 and then the subsequent C-Se bond scission rather than the opening of dithiole ring would lead to the formation of N-aryl or alkyl substituted 1,2-dithiole-3-imine (III-S).



Similarly, when the imide (I) was treated with an equimolar amount of p-chlorobenzenethiol in CH_3CN at room temperature or H_2S gas was bubbled into the imide-suspended CH_3CN solution, the rearranged N-benzenesulfonyl-1,2-thiaselenole-3-imine (II-Se) was obtained in a moderate yield. In addition, a minor amount of selenium-unmigrated N-benzenesulfonyl-1,2-dithiole-3-imine (II-S) was formed like in the reaction with amines.

Thus the reaction is considered to proceed through the initial formation of the addition complex of I and mercaptan on the tetravalent selenium atom and the subsequent formation of the ion-pair (V), which receives the nucleophilic addition of the amide anion on carbon-3 to form a tetrahedral intermediate (VI), that eventually leads to the formation of II.



Inspection of the data in Table I indicates that, like in the reaction with amines, the formation of (II-Se) is preferred to that of the corresponding sulfur analogue (II-S) even in the reaction with mercaptans. This finding could reasonably be accounted for by the assumption that the in-ring C-S bond in VI can assume the more suitably oriented anti conformation to be broken than that of C-Se bond; namely the C-S bond is nearly anticoplanar to N-H bond while the C-Se bond is perpendicular, as shown below:

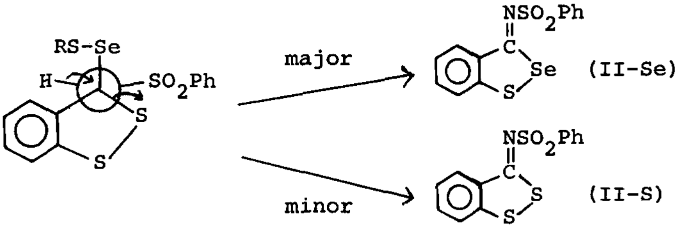
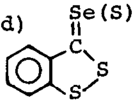


Table I. Reactions of (I) with Amines and Mercaptans in CH_3CN at Room Temperature.

reagent				Product (% yield)			
	III-S	II-Se	II-S	$PhSO_2Ph$	S_x		Se_x
$p\text{-}Cl\text{-}C_6H_4\text{-}NH_2$	58.6	6.7	2.2	89.0	a)	10.3	81.2
$t\text{-}BuNH_2$	90.2	1.5	1.3	85.8	a)	4.0	85.0
$p\text{-}Cl\text{-}C_6H_4\text{-}SH$	-	16.2	trace	41.0	a)	56.1	a)
H_2S	-	24.7	6.4	35.9	19.0	52.0 (3.9)	a)

a) no attempt to determine the yield was made.

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