FORMATION AND RECYCLIZATION OF HETEROCYCLES

XII.* SYNTHESIS AND TRANSFORMATIONS OF 4-THIOXOSELENAZOLIDIN-2-ONE

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The reaction of 1,3-selenazolidine-2,4-dione with P_2S_5 in absolute dioxane has given 4-thioxoselenazolidin-2-one, which is readily recyclized under the action of hydrazine and arylhydrazines into the corresponding triazolinones. With aromatic amines and with methylhydrazine, only condensation at the thione group takes place.

We have shown previously that azolidinones containing an oxygen or sulfur atom in the heterocycle recycle under the action of hydrazine or its substituted derivatives into triazolinones [2] or triazolinethiones [3]. In the case of 4-thioxothiazolidin-2-one, recyclization takes place through a stage of the formation of intermediate 4-hydrazinothiazolidin-2-ones, which isomerize into triazolinones both under the influence of heat and in the presence of nucleophilic reagents [4]. Continuing an investigation in this direction, we have performed experiments on the hydrazination of 4-thioxoselenazolidin-2-one.

The initial 4-thioxoselenazolidin-2-one (II) was obtained by the sulfuration reaction of 1,3-selenazolidine-2,4-dione (I) with phosphorus pentasulfide in absolute dioxane by analogy with the work of Grishchuk et al. [5]. The sulfuration reaction takes place extremely smoothly, although the end-product is highly contaminated with metallic selenium, from which it can be freed by crystallization from benzene. The reaction of 4-thioxoselenazolidin-2-one (II) with hydrazine, which is accompanied by the evolution of hydrogen sulfide, takes place fairly vigorously even when the reaction mixture is cooled to 0°C. The product obtained as a result of the reaction does not exhibit properties characteristic for compounds containing a free hydrazine group. It does not give the reactions for the hydrazine group with Fehling's reagent, does not react with benzaldehyde, and is not hydrolyzed on being boiled with concentrated hydrochloric acid. On the basis of its analytical characteristics and physicochemical properties the structure of the triazolinone (III) containing a hydroseleno group in the side chain is proposed for the compound obtained. On storage in the air, and even more rapidly on heating in DMFA, the product undergoes oxidation with the formation of the diselenide (IV). Compounds (V and VI) with similar properties are obtained by the reaction of (II) with arylhydrazines. Thus, in the case of 4-thioxoselenazolidin-2-one its reaction with hydrazines is completed by the recyclization of the selenazolidine ring into a triazoline ring with the avoidance of the stage of the formation of a hydrazone (as was the case with the thiazolidines [4]). The reaction probably takes place through a stage of the quasi-1,2-addition of the hydrazine molecule to the heterocycle [6, 7], and the splitting out of hydrogen sulfide takes place after the cleavage of the selenazolidine ring.

In the reaction of methylhydrazine with 4-thioxoselenazolidin-2-one the recyclization on reaction discussed does not take place, and only 4-(α-methylhydrazine)selenazolin-2-one (VII) is formed. In all probability, the splitting out of hydrogen sulfide takes place somewhat faster here and there is not sufficient time for attack in position 2 of the heterocycle leading to the production of the triazoline system.

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[*] For communication XI, see [1].

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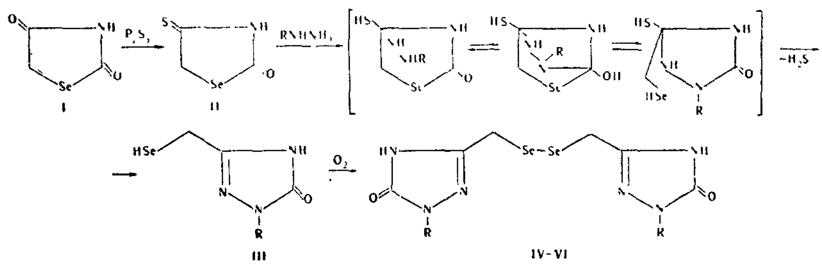
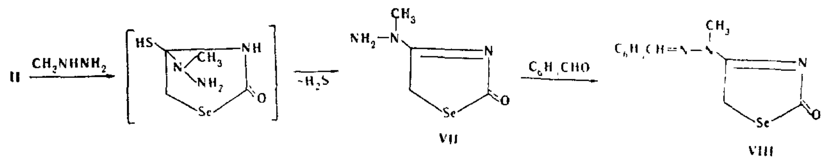
TABLE 1. 4-Aryliminoselenazolidin-2-ones

Compound	Ar	Mp, °C (from butanol)	Empirical formula	N, % found	N, % calculated	Yield, %
X	*p*-$CH_3C_6H_4$	298—299	$C_{10}H_{10}N_2OSe$	11,3	11,1	63
XI	*p*-ClC_6H_4	251—252	$C_9H_7N_2OSeCl$	10,1	10,0	53
XII	*p*-BrC_6H_4	242—243	$C_9H_7N_2OBrSe$	8,7	8,8	49
XIII	*o*-$CH_3OC_6H_4$	222—223	$C_{10}H_{10}N_2O_2Se$	9,8	10,0	58
XIV	α-Naphthyl	302—303	$C_{13}H_{10}N_2OSe$	9,6	9,7	83

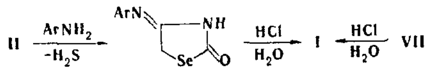


III R = H, IV R = H; V R = C_6H_5, VI R = p-$NO_2C_6H_4$

In an attempt to recyclize the azolinone (VII) in the presence of nucleophiles by analogy with previous work [4], only the oxidative cleavage of the selenazoline ring with the liberation of metallic selenium was observed. This even takes place when the reaction is performed in an inert-gas atmosphere.



The condensation of 4-thioxoselenazolidin-2-one at the thione group with aromatic amines takes place similarly. The Schiff's bases (IX-XIV) (see Table 1) are obtained in good yield. In order to prove the structure of these compounds, they were subjected to acid hydrolysis by being boiled in concentrated hydrochloric acid. The hydrolysis product proved to be 1,3-selenazolidine-2,4-dione (I). Compound (I) was also obtained by the acid hydrolysis of the azolinone (VII):



In the IR spectra of the triazolinones (III-VI) and the azolinone (VII) taken in KBr tablets the difference in their structures appears clearly. The triazolinones (III-VI) give a broad band in the 3400-3450-cm^{-1} region which is characteristic for the stretching vibrations of NH in a triazoline ring. In the case of the azolinone (VII), ν_{NH} appears in the form of two bands at 3230 and 3315 cm^{-1}. The band of the stretching vibrations of the carbonyl group ($\nu_{C=O}$ 1670 cm^{-1}) is shifted by 40-50 cm^{-1} in the short-wave direction in (VII) as compared with the triazolinones (III-VI).

EXPERIMENTAL

4-Thioxoselenazolidin-2-one (II). A solution of 1.64 g (10 mmoles) of 1,3-selenazolidine-2,4-dione in 20 ml of sodium-dehydrated freshly distilled dioxane was treated with 2.5 g (11 mmoles) of P_2S_5, and the mixture was boiled with stirring for 2 h. Then the solid matter was filtered off, the dioxane was distilled off from the filtrate in vacuum, and the residue was treated with water. The precipitate that deposited was filtered off. Yield 1.6 g (89%), mp 164°C (decomp., from benzene). Brown crystals soluble in acetone and chloroform, less soluble in ethanol, dichloroethane, and benzene, and insoluble in water. Found, %: S 17.9; Se 44.0. C_3H_3NOSSe. Calculated, %: S 17.8; Se 43.8.

5-(α-Hydroselenomethyl)-1,2,4-triazolin-3-one (III). With cooling to 0°C, an equimolar amount of hydrazine hydrate was added to a suspension of 4-thioxoselenazolidin-2-one in ethanol. When the temperature was raised to that of the room, hydrogen sulfide was evolved and a precipitate was formed which was filtered off and was washed with methanol and ether. Yield 55-60%; the substance showed no mp but darkened at 250°C. It did not give a positive reaction with Fehling's reagent for a hydrazine group, did not react with benzaldehyde, and underwent no change on being boiled in concentrated hydrochloric acid. Bright-yellow crystals insoluble in alcohols, dioxane, and ether, soluble in water on heating. Found, %: C 20.5; H 3.0; N 23.5; Se 44.7. $C_3H_5N_3OSe$. Calculated, %: C 20.2; H 2.8; N 23.6; Se 44.4.

Di(5-oxo-1,2,4-triazolin-3-ylmethyl) diselenide (IV) was formed when the triazolinone (III) was stored in the air or when it was heated in DMFA at 100-110°C for 3 h. The yield was quantitative of a substance which did not melt below 330°C and then darkened. Yellow crystals insoluble in alcohols, water, and dioxane and soluble on heating in DMFA, undergoing no change on being boiled in concentrated hydrochloric acid. Found, %: C 20.5; H 2.5; N 23.6; Se 45.0. $C_6H_8N_6O_2Se_2$. Calculated,%: C 20.3; H 2.3; N 23.7; Se 44.6.

Di(5-oxo-1-phenyl-1,2,4-triazolin-3-ylmethyl) Diselenide (V). An equimolecular amount of phenylhydrazine was added to a suspension of the selenazolidinone (II) in ethanol cooled to 0°C. Then the temperature was raised to that of the room and after 30 min the precipitate that had deposited was filtered off. Yield 70-75%, mp 206°C (from aqueous dimethylformamide). Yellow crystals insoluble in alcohols and water, soluble in dimethylformamide, undergoing no change on being boiled in concentrated hydrochloric acid and not being oxidized on being heated in DMFA. Found, %: C 42.8; H 3.3; N 16.3; Se 31.5. $C_{18}H_{16}N_6O_2Se_2$. Calculated, %: C 42.7; H 3.2; N 16.6; Se 31.2.

Di[5-oxo-1-(p-nitrophenyl)-1,2,4-triazolin-3-ylmethyl] diselenide (VI) was obtained by boiling equimolecular amounts of the selenazolidinone (II) and p-nitrophenylhydrazine for 15 min. Yield 67%, mp 279-280°C (from butanol). Light-yellow crystals insoluble in water, sparingly soluble in butanol, and undergoing no change on being boiled in concentrated hydrochloric acid. Found, %: C 35.9; H 2.5; Se 26.6. $C_{18}H_{14}N_8O_6Se_2$. Calculated, %: C 36.2; H 2.4; Se 26.5.

4-(α-Methylhydrazino)-Δ^3-1,3-selenazolin-2-one (VII) was obtained by mixing equimolecular amounts of the selenazolidinone (II) and methylhydrazine in ethanol at a temperature of about 0°C with the subsequent raising of the temperature to that of the room. Yield 47-50%, mp 143°C (decomp., from ethanol). Colorless crystals soluble on heating in water and ethanol. When these solutions were heated for only 10-15 min, a black precipitate of metallic selenium deposited. The substance did not give a positive reaction for a hydrazine group with Fehling's reagent. Found, %: C 25.4; H 4.0; N 22.1; Se 41.2. $C_4H_7N_3OSe$. Calculated, %: C 25.0; H 3.6; N 21.9; Se 41.4.

4-(Benzylidene-α-methylhydrazino)-Δ^3-1,3-thiazolin-2-one (VIII) was formed by the brief heating of the hydrazone (VII) with an equimolecular amount of benzaldehyde in ethanol. Yield 93%, mp 195-196°C (from ethanol). Colorless crystals insoluble in water and soluble on heating in ethanol and dioxane. Found, %: N 14.9. $C_{11}H_{11}N_2OSe$. Calculated, %: N 15.0.

4-(Phenylimino)selenazolidin-2-one (IX). To a suspension of 1.8 g (10 mmoles) of the selenazolidinone (II) in 10 ml of ethanol was added 0.93 g (10 mmoles) of freshly distilled aniline, and the mixture was heated in the water bath for 30 min. The precipitate was filtered off and was washed with ethanol and ether. Yield 1.4 g (54%), mp 230-231°C (from butanol). Colorless crystals soluble on heating in butanol and DMFA. Found, %: N 12.0. $C_9H_8N_2OSe$. Calculated, %: N 11.8.

Compounds (X-XIV) were obtained similarly.

1,3-Selenazolidine-2,4-dione (I) was obtained by boiling the azolinone (VII) or compound (IX) in concentrated hydrochloric acid for 3 h. Yield 85-90%, mp 147°C (from water) (literature [8]: 147°C). It gave no depression of the melting point with an authentic sample.

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