SYNTHESIS AND STUDY OF 2-ARYLAMINOSELENAZOLINES

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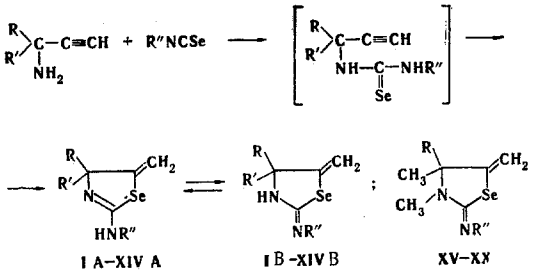
2-Arylamino-2-selenazolines were obtained by reaction of primary 2-alkynylamines with aryl isoselenocyanates. It was established that 2-benzylaminoselenazolines have amine structures, while in the case of 2-arylaminoselenazolines the tautomeric equilibrium is shifted to favor the imine form.

2-Aminoselenazoline derivatives have been previously obtained by condensation of α-halo carboxylic acids with selenourea or its derivatives [1, 2]. We have found a possibility for the synthesis of selenazolines by reaction of 2-alkynylamines with isoselenocyanates.

In all likelihood, the reaction of aryl isoselenocyanates with 2-alkynylamines proceeds in analogy with the reaction of isothiocyanates [3], i.e., through the intermediate formation of selenoureas. However, we were unable to isolate 2-propynylselenoureas: the latter undergo cyclization during the reaction to give the corresponding selenazolines. The reaction of isoselenocyanates with 2-propynylamines proceeds more vigorously than the reaction with the corresponding isothiocyanates and requires considerable cooling and dilution of the reagents with organic solvents (benzene). Primary 2-alkynylamines react to give ring nitrogen-unsubstituted selenazolines (I-XIV), whereas secondary amines give 3-alkyliminoselenazolidines (XV-XX, Table 1).

The formation of selenazolines was monitored from the appearance in the IR spectra of I-XIV of absorption bands of a methylene group at 1610 and 3100 cm^{-1}. Cyclization to five-membered rings was proved by the PMR spectra: the formation of selenazolines was accompanied by the appearance in the spectra of two doublet signals of methylene protons at ~5.1 and 5.3-5.5 ppm (J = 2 Hz).



IA-XIVA IB-XIVB XV-XX

The signals of the methylene protons of the selenazolines are shifted to weaker field as compared with the analogous signals of thiazolines; this is due to the anisotropic effect of the selenium atom. The latter may also explain the increase in the nonequivalence of the geminal protons in selenazolines, which is expressed as an increase in the difference in the chemical shifts of the methylene protons as compared with thiazolines.

The possibility of obtaining 2-iminoselenazolidines with known structures (XV-XX) enables one to investigate the tautomeric forms of the selenazolines obtained. We assigned amine and imine structures as a function of the substituents in the amino group by means of UV, IR, and PMR spectroscopy.

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TABLE 1. 2-Aminoselenazolines (I-XIV) and 2-Iminoselenazolidines (XV-XX)

Compound	R*	R″	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
I	CH_3	C_6H_5	185	54,1	5,0	10,8	$C_{12}H_{14}N_2Se$	54,3	5,3	10,6	87
II	C_2H_5	C_6H_5	130	55,4	5,7	10,0	$C_{13}H_{16}N_2Se$	55,9	5,7	10,0	65
III	C_3H_7	C_6H_5	135	56,2	6,2	9,6	$C_{14}H_{18}N_2Se$	57,3	6,1	9,6	63
IV	$(CH_2)_5$	C_6H_5	168—169	58,9	6,3	9,6	$C_{15}H_{18}N_2Se$	59,0	5,9	9,2	53
V	CH_3	$C_6H_4CH_3$-*p*	155	55,6	6,4	10,0	$C_{13}H_{16}N_2Se$	55,9	5,7	10,0	81
VI	C_2H_5	$C_6H_4CH_3$-*p*	155	57,5	6,7	9,5	$C_{14}H_{18}N_2Se$	57,3	6,1	9,6	69
VII	$(CH_2)_5$	$C_6H_4CH_3$-*p*	172	60,5	5,8	8,6	$C_{16}H_{20}N_2Se$	60,2	6,2	8,8	66
VIII	CH_3	$C_6H_4OCH_3$-*p*	165	53,7	5,2	10,2	$C_{13}H_{16}N_2OSe$	52,9	5,4	9,5	79
IX	C_2H_5	$C_6H_4OCH_3$-*p*	160	54,9	6,3	9,3	$C_{14}H_{18}N_2OSe$	54,4	5,8	9,1	67
X	$(CH_2)_5$	$C_6H_4OCH_3$-*p*	195	57,6	6,4	8,1	$C_{16}H_{20}N_2OSe$	57,3	6,0	8,4	53
XI	CH_3	$CH_2C_6H_5$	95	55,3	5,6	10,7	$C_{13}H_{14}N_2Se$	55,9	5,7	10,0	71
XII	C_2H_5	$CH_2C_6H_5$	92	57,2	5,9	9,5	$C_{14}H_{18}N_2Se$	57,3	6,1	9,6	82
XIII	C_3H_7	$CH_2C_6H_5$	105	58,1	6,0	8,4	$C_{15}H_{20}N_2Se$	58,6	6,5	9,1	63
XIV	$(CH_2)_5$	$CH_2C_6H_5$	143—145	59,8	6,2	8,4	$C_{16}H_{20}N_2Se$	60,2	6,3	8,8	55
XV	CH_3	C_6H_5	63	56,1	6,3	10,2	$C_{13}H_{16}N_2Se$	55,9	5,7	10,0	78
XVI	C_2H_5	C_6H_5	72	57,3	6,2	9,6	$C_{14}H_{18}N_2Se$	57,3	6,1	9,6	93
XVII	CH_3	$CH_2C_6H_5$	58	57,4	5,7	—	$C_{14}H_{18}N_2Se$	57,3	6,1	—	93
XVIII	C_2H_5	$CH_2C_6H_5$	60	58,9	6,2	—	$C_{15}H_{20}N_2Se$	58,6	6,5	—	80
XIX	CH_3	$C_6H_4CH_3$-*p*	100	57,1	6,4	—	$C_{14}H_{18}N_2Se$	57,3	6,1	—	83
XX	C_2H_5	$C_6H_4CH_3$-*p*	107	58,5	6,0	9,9	$C_{15}H_{20}N_2Se$	58,6	6,5	8,8	85

* In all of the compounds except IV, VII, X, and XIV, R′ = CH_3; in IV, VII, X, and XIV, R + R′ = $(CH_2)_5$.

TABLE 2. IR and UV Spectra of Selenazolines

Compound	IR spectra, ν, cm^{-1}		UV spectra	
	C=C	C=N	Solvent	λ, nm (ε · 10^{-3})
I	1595, 1615	1670	Alcohol	204 (3,5), 246 (2,5)
II	1595, 1615	1650	Alcohol	204 (3,4), 246 (2,6)
			Hexane	202 (3,35), 247 (2,75)
IV	1590, 1610	1640	Alcohol	204 (4,6), 238 (3,2)
VI	1600	1640	Alcohol	206 (3,5), 247 (2,75)
			Hexane	204 (4,9), 248 (4,0)
			Alco.+H_2SO_4 (10%)	224 (3,9), 238 (2,6)
XI	1600	1550	Alcohol	205 (3,62), 238 (2,66), 299 (1,33)
			Hexane	201 (5,25), 248 (3,35), 308 (1,6)
XII	1600	1550	Alcohol	208 (3,5), 238 (2,23), 299 (1,16)
			Hexane	200 (4,40), 248 (2,7), 308 (1,6)
			Alco.+H_2SO_4 (10%)	229 (2,3), 318 (1,35)
XIII	1600	1550		
XIV	1600	1550		
XV	1590, 1620	1640	Alcohol	205 (4,1), 237 (2,7)
XVI	1590, 1610	1640	Alcohol	204 (4,0), 232 (2,45)
XVII	1615	1550	Alcohol	211 (2,24),
XVIII	1615	1550	Alcohol	211 (2,44)

TABLE 3. PMR Spectra of Selenazolines, δ, ppm

Compound	R	4-CH_3	NH or 3-CH_3	R″		=C<H*/H
				CH_3, $—CH_2—$	C_6H_5	
II	0,87 t, 1,48 q	1,25	8,70	—	7,10 m	5,05; 5,28
VI	0,80 t, 1,47 q	1,18	7,80	2,24 s	6,91 m	5,07; 5,30
XI	1,5 s	1,25	5,74	4,77 d (4)	7,20 s, 7,27 s	5,00; 5,26
XII	0,60 t, 1,50 m	1,16	5,76	4,80 d (4)	7,25 s, 7,33 s	5,06; 5,23
XVI	0,80 t, 1,72 q	1,32	2,90	—	6,95 m	5,09; 5,36
XVII	1,36 s	1,36	2,90	4,25 s	7,30 s	5,17; 5,53
XVIII	0,82 t, 1,70 q	1,34	2,90	4,24 s	7,28 s	5,28; 5,50

* The chemical shifts of two doublet signals (J = 2 Hz) are indicated.

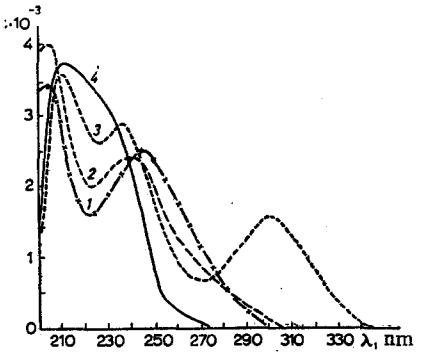

Fig. 1. UV spectra in alcohol: 1) 2-phenylimino-4-methyl-4-ethyl-5-methyleneselenazolidine (II); 2) 2-phenylimino-3,4-dimethyl-4-ethyl-5-methyleneselenazolidine (XVI); 3) 2-benzylamino-4,4-dimethyl-5-methyleneselenazoline (XI); 4) 2-benzylimino-3,4,4-trimethyl-5-methyleneselenazolidine (XVII).

UV Spectra

The absorption spectra of 5-methylene-2-arylaminoselenazolines differ as a function of the substituents attached to the amino group. The N-aryl derivatives (I-X) have two absorption maxima at 204-206 and 238-248 nm (Table 2), while the N-benzyl compounds (XI and XII) have three maxima at 205-208, 240, and 300 nm. The long-wave absorption bands are due to $n \rightarrow \pi^*$ transitions: A typical bathochromic shift is observed for them on passing from alcohol solutions to hexane solutions. From the changes in the position of the absorption bands on passing from hexane solutions to alcohol solutions and on passing to the sulfate salts one can also assign the absorption maxima in the short-wave region to transitions with the participation of the n electrons [4].

The absorption spectra of the N-aryl derivatives (I-X) are similar to the spectra of 2-aryliminoselenazolidines (XV and XVI). The 2-benzyliminoselenazolidines (XVII and XVIII) have one maximum, while the N-benzyl derivatives with nonfixed structures (XI and XII) have three absorption maxima (Fig. 1). These observations can be explained by the fact that the N-benzyl compounds exist in the amine form (XIA and XIIA), whereas the N-aryl compounds exist in the 2-aryliminoselenazolidine form (IB-XB).

It should be noted that the overall trend of the absorption curves that we obtained for 2-benzylamino-4-alkyl-5-methyleneazolines coincides with the absorption curves presented in [5] for 5-phenyl-2-aminoselenazolines in the imine and amine forms: Rapidly falling curves for the imine form and two distinct absorption maxima for the amine form (the spectra in [5] were recorded up to 210 nm).

IR Spectra

Two intense absorption bands at 1590-1620 and 1640-1670 cm^{-1} are characteristic for most of the selenazolines at 1500-1700 cm^{-1} (Table 2). We assigned the first absorption bands to vibrations of the $C{=}CH_2$ group and the phenyl ring: It remains unchanged in the case of compounds with amine and imine forms. We assigned the intense band at 1640-1670 cm^{-1} to the vibrations of the C=N bond [6]. The presence of this band in the spectra of iminoselenazolidines (XV and XVI) provides a basis for its assignment to the vibrations of the exocyclic C=N group. The presence of this band in the spectra of the N-aryl derivatives (I-X) also makes it possible to assume an imine structure (B) for these compounds [7].

In addition to an absorption band at 1615 cm^{-1} (C=C), a band of an exocyclic C=N bond at 1650 cm^{-1} is present in the spectra of 2-benzyliminoselenazolidines (XVII and XVIII) (Table 2). Absorption is absent at 1630-1670 cm^{-1} in the case of 2-benzylaminoselenazolines (XI-XIV) without substituents attached to the ring nitrogen atom, but a band appears at 1550 cm^{-1}. We assigned the latter to the stretching vibrations of the endocyclic C=N group of the selenazoline ring; this confirms the amine structure (A).

The PMR spectra do not give additional data for the assignment of tautomeric forms of 2-arylaminoselenazolines. One's attention is directed to the considerable shift to weak field of the signal of the proton of the NH group of aryl-substituted selenazolines; this signal is observed at 8.5-9.0 ppm, as compared with 5.0-6.0 ppm for benzyl derivatives.

The use of PMR spectroscopy was successful in the assignment of the tautomeric forms of N-benzylaminoselenazolines (XI-XIV). The singlet at 4.2 ppm corresponds to the protons of the $N-CH_2$ group of the 2-benzyliminoselenazolidines. In the case of benzyl derivatives with a nonfixed structure (XI-XIV) this signal is shifted 0.5 ppm to weak field and appears as a doublet at 4.77 ppm with J = 4 Hz. The difference in the chemical shifts of the protons of the $N-CH_2$ group is explained by the different effect on them of the exocylic nitrogen atom in the amine and imine forms and proves an amine structure (A) for XI-XIV (Table 3). In the case of freshly prepared XI the chemical shift of the N-methylene protons coincides with the chemical shifts for the imine models (4.27 ppm). However, after 8 months the same sample gave a signal of a methylene proton at 4.77 ppm; this constitutes evidence for tautomeric conversion to the aminoselenazoline form (XIA). It is interesting to note that the imine form of the thiazoline analog of XI is more stable than the amine form.

The studies make it possible to conclude that N-aryl derivatives have 2-aryliminoselenazolidine structures (IB-XB) and that the N-benzyl compounds are more stable in the 2-benzylaminoselenazoline form (XIA-XIVA).

EXPERIMENTAL

The UV spectra of the compounds were recorded with a Specord UV-vis spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of 10% solutions of the compounds in CCl_4 were obtained with a ZKR-60 spectrometer (Carl Zeiss) with an operating frequency of 60 MHz with hexamethyldisiloxane as the internal standard.

2-Phenylimino-3-methyl-4,4-dimethyl-5-methyleneselenazolidine (XV). A solution of 1.27 g (7 mmole) of phenyl isoselenocyanate in 3 ml of absolute benzene was added dropwise with stirring and cooling to 0°C to 0.68 g (7 mmole) of 3-methylamino-3-methyl-1-butyne, and the mixture was maintained at room temperature for 1 h and at 40°C for 1 h. The solvent was removed by distillation, and the residue was recrystallized from petroleum ether to give 2.2 g (78.4%) of a product with mp 63°C and R_f 0.46 (with Al_2O_3 as the adsorbent and benzene as the eluent).

Compounds I-XX (Table 1) were obtained by a similar method; I-XVIII were crystallized from heptane or methanol, and XIX and XX were crystallized from CCl_4. Compound XVIII was initially isolated in the form of an oil, which was purified by chromatography with a column filled with Al_2O_3 (elution with benzene, R_f 0.40); the oil crystallized in the course of a month (mp 60°C).

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