

Synthesis of tetrahydro-1,3,5-selenodiazine-2-selenones

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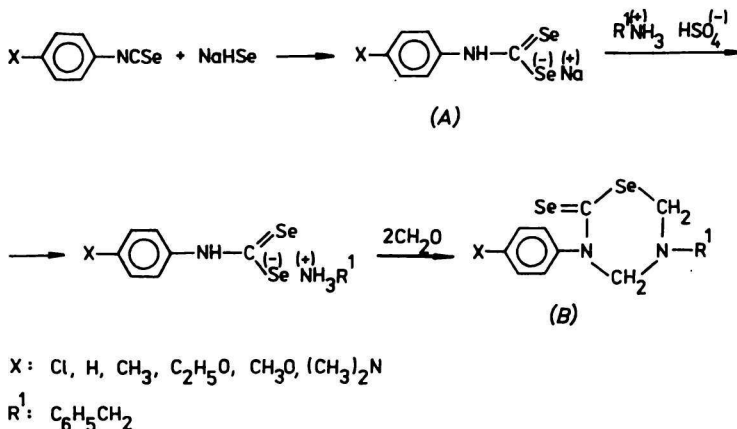
Phenyl isoselenocyanates in nucleophilic addition of sodium hydrogen selenide in the presence of salt of primary amine and formaldehyde react under the formation of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones. The structures of the synthesized compounds were proved by i.r., u.v., and $^1\text{H-n.m.r.}$ spectra.

Фенилизоселеноцианаты при нуклеофильном присоединении гидрогенида натрия в присутствии соли первичного амина и формальдегида реагируют с образованием 3,5-замещенных тетрагидро-1,3,5-селенодiazин-2-селенонов. Структура синтезированных соединений доказана ИК, УФ и $^1\text{H-NMR}$ спектрами.

In our previous works we have studied the reactions of phenyl isoselenocyanates with diazomethane, enamines, n-butylamine, and methyl 3-mercaptopropionate [1, 2]. From the results obtained it follows that phenyl isoselenocyanates enter nucleophilic addition reactions easily. The rate of these reactions increases with the increasing electron-accepting nature of the substituent. The reactions of phenyl isoselenocyanates with sodium hydrogen selenide have not been studied so far. In the synthesis of 3,5-disubstituted selenodiazines [3] by addition of carbon selenide to amine in the presence of formaldehyde we have found that this method is considerably limited to strongly basic amines.

The subject of the present work was the preparation of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones by nucleophilic addition of sodium hydrogen selenide to phenyl isoselenocyanates in the presence of salt of primary amine and formaldehyde according to Scheme 1.

For the synthesis the modified method for the preparation of thiadiazines was used [4]. On the basis of the obtained results in the synthesis of 3,5-disubstituted derivatives of tetrahydro-1,3,5-selenodiazine-2-selenones by addition-cyclization reaction of phenyl isoselenocyanates with sodium hydrogen selenide it can be assumed that the low yields (Table 1) are due to the instability of diselenocarbamate which easily decomposes to the appropriate isoselenocyanate. The best yields were obtained in the case when phenyl isoselenocyanate containing an electron-accepting substituent was used for the addition-cyclization reaction.



Scheme 1

Table 1

Characteristics and yields of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones

Compound	X	Formula	M	Calculated/found			Yield %	M.p. °C
				% C	% H	% N		
I	Cl	C ₁₆ H ₁₅ N ₂ Se ₂ Cl	428.68	44.82	3.52	6.54	42.0	132—133
				44.39	3.90	6.80		
II	H	C ₁₆ H ₁₆ N ₂ Se ₂	394.24	48.74	4.11	7.10	32.2	129—130
				49.07	4.34	6.91		
III	CH ₃	C ₁₇ H ₁₈ N ₂ Se ₂	408.26	50.01	4.44	6.86	35.5	125—126
				49.34	4.70	6.83		
IV	C ₂ H ₅ O	C ₁₈ H ₂₀ N ₂ OSe ₂	438.29	49.33	4.59	6.39	39.7	127—128
				49.59	4.38	6.23		
V	CH ₃ O	C ₁₇ H ₁₈ N ₂ OSe ₂	424.26	48.12	4.27	6.60	35.4	135—136
				47.89	4.39	6.83		
VI	(CH ₃) ₂ N	C ₁₈ H ₂₁ N ₃ Se ₂	437.30	49.44	4.84	9.61	21.7	137—138
				49.64	5.15	10.01		

The skeleton of the synthesized tetrahydro-1,3,5-selenodiazine-2-selenones appeared in the i.r. and u.v. spectra similarly as that of the derivatives described in [3]. The synthesized 3,5-disubstituted selenodiazines exhibited intensive absorption bands at 1400 cm⁻¹ which were attributed to the atomic grouping >N—C=Se (Table 2) on the basis of analogy with the corresponding sulfur compounds [4].

Table 2

Infrared (cm^{-1}), ultraviolet (nm), and nuclear magnetic resonance (p.p.m.) spectral data of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenone

Compound	X	$\nu(=\text{N}-\overset{\text{I}}{\text{C}}=\text{Se})$	$\lambda_{\text{max I}}$ $\log \epsilon$	$\lambda_{\text{max II}}$ $\log \epsilon$	$\lambda_{\text{max III}}$ $\log \epsilon$	τ_A	τ_B	τ_C	τ_X
I	Cl	1464	239	298	340	5.38	5.34	5.89	—
		1317	4.52	4.11	3.57				
II	H	1475	237	265	342	5.30	5.30	5.85	—
		1310	4.39	4.30	4.29				
III	CH_3	1467	236.5	292	340	5.38	5.38	5.88	7.64
		1317	4.43	4.00	3.76				
IV	$\text{C}_2\text{H}_5\text{O}$	1472	231	270	341	5.38	5.38	5.88	5.98
		1310	4.29	3.97	3.90				
V	CH_3O	1475	243	290	340	5.38	5.38	5.88	6.19
		1310	4.34	4.06	3.79				
VI	$(\text{CH}_2)_2\text{N}$	1466	230	265	326.5	5.39	5.39	5.89	7.04
		1313	3.86	3.62	4.04				

The u.v. spectral data of the studied selenodiazines are presented in Table 2. On the basis of comparison of the u.v. spectra of the synthesized selenodiazines with those of N,N' -disubstituted selenoureas ($\lambda_{\text{max I}} = 208 \text{ nm}$, $\log \epsilon_1 = 4.30$; $\lambda_{\text{max II}} = 280 \text{ nm}$, $\log \epsilon_2 = 4.15$) we attributed the absorption band of selenodiazines at 260–290 nm to "N" conjugation and that at 340 nm to "Se" conjugation [3].

In the ^1H -n.m.r. spectra of the appropriate compounds (Table 2) two singlets belonging to three methylene groups (A , B , C) appeared in the region of 5–6 τ with the derivatives II — VI contrary to selenodiazines with the same substituents in the positions 3, 5 [3]. In the case of the derivatives mentioned above the skeletal methylene groups (A , B) appeared in the ^1H -n.m.r. spectrum as chemically equivalent ($\tau_A = \tau_B$). They can be distinguished only in the case of a stronger electron-accepting substituent such as chlorine, appearing in the ^1H -n.m.r. spectrum as a splitting ($\tau_A = 5.38$, $\tau_B = 5.34$). The protons of the 4-substituted aromatic ring of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones give a symmetric quartet which can be analyzed as a spectrum of the AB type [5]. Linear correlation between chemical shifts of skeletal methylene groups (A , B) and chemical shifts of protons of the aromatic ring with the Hammett constants has not been found.

Experimental

Infrared absorption spectra of the studied compounds were measured on a double-beam UR-20 (Zeiss, Jena) spectrophotometer in the region of 3600–700 cm^{-1} in KBr pellets (0.6 mg/300 mg KBr). The apparatus was calibrated by polystyrene foil.

Ultraviolet absorption spectra of the compounds investigated were measured on a recording Perkin—Elmer 402 spectrophotometer in the region of 210—400 nm at 5×10^{-5} M in dioxan using cells of 10 mm thickness.

Nuclear magnetic resonance spectra were obtained on a BS 487 A spectrometer at working frequency of 80 MHz. The compounds were measured in deuteriochloroform using tetramethylsilane as internal standard.

4-Substituted phenyl isoselenocyanates were prepared by addition of selenium to isonitriles [6, 7].

The ethanol solution of sodium hydrogen selenide was prepared by the reaction of sodium tetrahydridoborate with powdery selenium in ethanol [8].

Benzylammonium sulfate was prepared by the reaction of benzylamine with sulfuric acid in benzene with excess of benzylamine.

N,N'-Disubstituted selenoureas were prepared by the reaction of equimolar amounts of *n*-butylamine with the appropriate phenyl isoselenocyanate in ether solution. *N*-(4-Chlorophenyl)-*N'*-(*n*-butyl)selenourea, m.p. 120—121°C (chloroform—petroleum ether). UV spectrum (methanol): $\lambda_{\max I} = 209$ nm, $\log \epsilon_1 = 4.27$; $\lambda_{\max II} = 286$ nm, $\log \epsilon_2 = 4.07$. For $C_{11}H_{15}ClN_2Se$ (289.6) calculated: 45.61% C, 5.22% H, 9.67% N; found: 45.26% C, 5.11% H, 9.80% N. *N*-(4-Dimethylaminophenyl)-*N'*-(*n*-butyl)selenourea, m.p. 104—105°C (chloroform—petroleum ether). UV spectrum (methanol): $\lambda_{\max I} = 207$ nm, $\log \epsilon_1 = 4.45$; $\lambda_{\max II} = 273$ nm, $\log \epsilon_2 = 4.37$. For $C_{13}H_{21}N_3Se$ (298.3) calculated: 52.34% C, 7.09% H, 14.08% N; found: 52.29% C, 7.07% H, 14.08% N.

3,5-Disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones (I—VI)

The solution of phenyl isoselenocyanate (0.002 mol) in ethanol (10 ml) was treated with ethanol solution of sodium hydrogen selenide (0.08 g Se, 0.08 g $NaBH_4$ in 10 ml ethanol) in nitrogen atmosphere under stirring at room temperature. To the reaction mixture benzylammonium sulfate (0.41 g; 0.002 mol) in water (5 ml) was added stepwise. Then 37% aqueous solution of formaldehyde (2.43 g; 0.03 mol) was added gradually under continuous stirring. After 1 h stirring at room temperature, the crude product was filtered off, washed with water, dried, and crystallized from the mixture of chloroform—petroleum ether.

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