Synthesis, properties, and reactions of heterodienes. III.* Some cycloaddition reactions of isoselenocyanates with enamines and diazomethane

G. SUCHÁR and P. KRISTIAN

Department of Organic Chemistry, Faculty of Natural Sciences, P. J. Šafárik University, 041 67 Košice

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Cycloaddition reactions of isoselenocyanates with enamines of the crotone type as well as with diazomethane were studied. With enamines, α,β-disubstituted selenocrotonanilides were obtained as resulting products. With diazomethane the resulting product (*N*-substituted 5-amino-1,2,3-selenodiazole) could be isolated only in the case of 4-chlorophenyl isoselenocyanate. The structures of the synthesized compounds were proved by infrared, ultraviolet, and nuclear magnetic resonance spectra. Preparation of the mentioned compounds and relation between their structures and spectral properties are discussed.

Up to the present, the reactions of isoselenocyanates were less studied than those of their sulfur and oxygen analogs because of their difficult preparation as well as instability against temperature and polar medium. There are reports in the literature on some nucleophilic addition reactions of isoselenocyanates with nitrogen-containing bases [1—3] and with alcohol [4].

Cycloaddition reactions of heterocumulenes, suitable for synthesis of different heterocyclic compounds, have become very important lately [5]. A great number of literature data concern also cycloaddition reactions of isothiocyanates, the properties of which are very similar to those of the corresponding isoselenocyanates as we have shown in our previous work [6]. For instance, reactions of isothiocyanates with enamines and with diazomethane are known. The active hydrogen in the molecule of enamines readily reacts with isothiocyanates in 1,2-cycloaddition reactions [7—9]. In the reaction of diazomethane with isothiocyanates cycloaddition proceeds on the double C=S bond giving *N*-substituted 5-amino-1,2,3-thiadiazoles [10]. We supposed that isoselenocyanates would react similarly as isothiocyanates considering the relationship between selenium and sulfur.

In this work we studied the reactivity of isoselenocyanates, their 1,2-cycloaddition reactions with enamines and with diazomethane as well as synthesis, structure, and spectral properties of the obtained products. Substituted aryl isoselenocyanates, ethyl β-aminocrotonate, 2-amino-2-penten-4-one, and diazomethane were used as starting compounds. The reactions could be demonstrated on Scheme 1.

Experimental

Isoselenocyanates, *i.e.* phenyl (b.p. 70°C/3 torr), 4-methylphenyl (m.p. 61.5—62.0°C), 4-methoxyphenyl (m.p. 48—49°C), 4-chlorophenyl (m.p. 70—71°C), and 4-dimethylaminophenyl (m.p. 100—101°C) isoselenocyanates were described in our previous work [6].

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Enamines, *i.e.* 2-amino-2-penten-4-one (b.p. 99°C/12 torr) and ethyl β-aminocrotonate (b.p. 105°C/15 torr) were obtained by condensation reactions of ethyl acetoacetate and acetylacetone, respectively, with ammonia [11]. *N*-Phenyl-2-amino-2-penten-4-one (m.p. 52°C) [4] and ethyl *N*-ethyl-β-aminocrotonate (b.p. 109°C/12 torr) were prepared according to [12, 13].

The solution of diazomethane in ether (63—70%) was prepared by decomposition of methylnitrosourea with 50% solution of potassium hydroxide at 5°C [14].

The i.r. spectra of α,β-disubstituted selenocrotonanilides were measured in the region of 3600—700 cm^{-1} on a double-beam UR-20 (Zeiss, Jena) spectrometer (concentration 0.05 M in chlorofor m) in NaCl cells of 0.17 mm thickness. The u.v. spectra of the studied compounds were taken on a Perkin—Elmer 402 spectrometer in the region of 210—400 nm at 20°C in 10-mm cells (concentration 5×10^{-5} M in methanol).

The n.m.r. spectra of 5-(4-chloroanilino)-1,2,3-selenodiazole were measured on a Tesla BS 487 A spectrometer in deuterated acetone at 80 MHz using tetramethylsilane (TMS) as internal standard.

α,β-Disubstituted selenocrotonanilides (I—V)

Enamine (0.003 mole) and isoselenocyanate (0.003 mole) were heated at 30°C for 10 min. The formed reddish viscous solution became a dark solid after staying for 1—2 days at room temperature. This product was dissolved in a small amount of chloroform, filtered and after addition of petroleum ether (b.p. 40—60°C), the appropriate α,β--disubstituted selenocrotonanilide crystallized.

5-(4-Chloroanilino)-1,2,3-selenodiazole (VI)

Into a flask provided with a stirrer and a dropping funnel absolute ether (20 ml) and 4-chlorophenyl isoselenocyanate (0.64 g; 0.003 mole) were added. This solution was cooled with dry ice in acetone (0 to −10°C) and the solution of diazomethane in ether (5 ml) was added dropwise. The product slowly precipitated from the solution and became dark. After 1-hr stirring, ether and the unchanged diazomethane were distilled off. The crude product was dissolved in chloroform on heating, purified with charcoal and after addition of petroleum ether a yellowish product precipitated on cooling. The pure product (0.2 g; 28%) of m.p. 133.0—133.5°C was obtained by repeated crystallization from chloroform.

For $C_6H_6N_3ClSe$ (258.57) calculated: 37.16% C, 2.33% H, 16.25% N; found: 36.80% C, 2.41% H, 15.95% N.

The i.r. (KBr) ν(C=C) = 1615 cm^{-1}; ($CHCl_3$) ν(NH) = 3410 cm^{-1}.

The u.v. (CH_3OH) $\lambda_{max\ I}$ = 225 nm (log ε_1 = 4.23), $\lambda_{max\ II}$ = 235 nm (log ε_2 = 3.64).

The n.m.r. (CD_3COCD_3) τ = 0.11 (NH), τ = 2.10 (CH), τ = 2.65 (H_{arom}).

Discussion

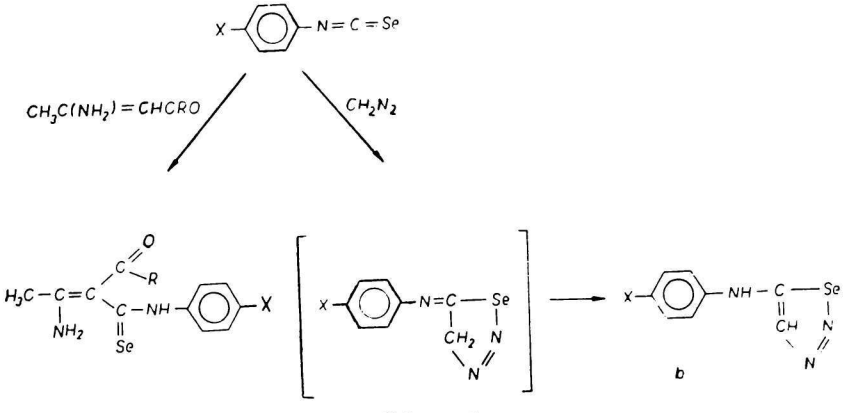
Synthesis of α,β-disubstituted selenocrotonanilides proceeded smoothly according to the Scheme 1*a* giving colour products in 60—70% yield (Table 1). The isolation of pure compounds was difficult because they easily liberated isoselenocyanate on heating even in weak polar solvents (chloroform) and because on reflux in ethanol selenium was split off. In the case of *N*-alkyl and *N*-aryl substituted enamines we failed to isolate the formed products in pure state. Though the spectral properties of these products corresponded to the assumed structure, elemental analyses did not prove that they were pure compounds.

Table 1

The synthesized α,β-disubstituted selenocrotonanilides

Compound	R X	Formula	*M*	Calculated/found % C	 % H	 %N	Yield [%] Colouring	M.p. [°C]
I	C_2H_5O H	$C_{13}H_{16}N_2O_2Se$	311.24	50.17 49.73	5.18 5.14	9.00 8.82	64.3 brownish--red	121—123
II	C_2H_5O CH_3	$C_{14}H_{18}N_2O_2Se$	325.27	51.69 51.38	5.57 5.70	8.61 8.61	61.5 orange	139—141
III	C_2H_5O CH_3O	$C_{14}H_{18}N_2O_3Se$	341.27	49.27 50.00	5.31 5.47	8.20 7.94	59.0 brownish--red	146—147
IV	CH_3 H	$C_{12}H_{14}N_2OSe$	281.20	51.25 50.89	5.02 5.04	9.96 9.68	59.5 red	135—137
V	CH_3 CH_3O	$C_{13}H_{16}N_2O_2Se$	311.24	50.16 50.57	5.18 5.50	9.00 9.25	75.0 orange	159—160

We chose isoselenocyanates with electron-accepting as well as electron-donating substituents (phenyl, 4-chlorophenyl, 4-methoxyphenyl, and 4-dimethylaminophenyl) for the reaction with diazomethane. A pure product was obtained only in the case of 4-chlorophenyl isoselenocyanate. Reactions of phenyl and 4-methoxyphenyl isoselenocyanates with the solution of diazomethane in ether gave a brownish-red paste. We failed to isolate a pure product from this paste by crystallization or chromatographic purification. Negative results were obtained also in the case when the reaction proceeded in the atmosphere of nitrogen. With 4-dimethylaminophenyl isoselenocyanate 40% of the starting compound was isolated from the reaction medium. It is evident from the mentioned facts that on synthesis of sele-

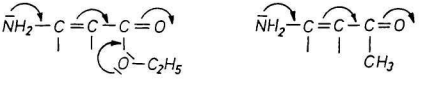


Scheme 1

R = C_2H_5O, CH_3O;
X = H, CH_3, CH_3O, Cl^-.

nodiazoles, two factors acted each against the other, *i.e.*, the reactivity of isoselenocyanates and instability of the formed products. The synthesis proceeded successfully in that case when the isoselenocyanate was ready enough to react with diazomethane and when its substituent did not hinder from aromatization of the primarily formed dihydroselenodiazole ring (Scheme 1*b*).

The i.r. spectra of the selenocrotonanilides (*I*—*V*) showed three significant absorption bands belonging to the mixed vibrations of —NH—C=Se group in the region of 1600—1000 cm^{-1} [15]. With the studied derivatives the absorption region of C=O and C=C bonds was interesting. The conjugation of carbonyl group with enamine systems was indicated by a strong shift of the ν(C=O) and ν(C=C) wavenumbers to lower values. With α-ethoxycarbonyl (*I*—*III*) derivatives (due to the disturbing ethoxy group) this shift was less significant (ν(C=O) $\sim$ 1665 cm^{-1}, ν(C=C) $\sim$ 1610 cm^{-1}) than with α-acetyl (*IV*, *V*) derivatives (ν(C=O) $\sim$ 1615 cm^{-1},



b

Scheme 2

ν(C=C) $\sim$ 1598 cm^{-1}) (Scheme 2, Fig. 1*a*, *c*, Table 2). The relative intensities of the appropriate absorption bands (Fig. 1) were in accordance with the mentioned facts. With α-ethoxycarbonyl derivatives (*I*—*III*), where the polarity of the C=C bond was greater than in the α-acetyl derivatives (*IV*, *V*) due to the disturbing

Table 2

Spectral data of α,β-disubstituted selenocrotonanilides

Compound	ν(NH—C=Se)	ν(C=C)	ν(C=O)	ν(NH)	λ_{max}	log ε
	1505			3505		
I	1260	1611	1665	3465	332	4.09
	1029			3350	309	4.11
	1518			3505		
II	1260	1611	1665	3465	335	4.13
	1035			3350	308	4.14
	1516			3505		
III	1260	1612	1665	3465	343	4.01
	1034			3350	299	4.09
	1504			3490		
IV	1258	1598	1617	3360	332	4.29
	1075			3160		
	1515			3490		
V	1255	1596	1615	3358	332	4.19
	1036			3160		

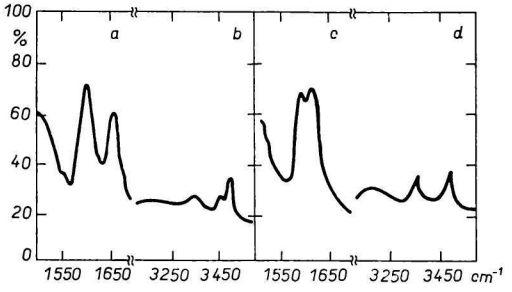
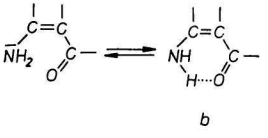


Fig. 1. Infrared absorption spectra.
a), *b*) β-Amino-α-ethoxycarbonyl(selenocroton)anilide (*I*); *c*), *d*) α-acetyl-β-amino(selenocroton)anilide (*IV*).

conjugation, the absorption ν(C=C) was more intensive than ν(C=O); with the α-acetyl derivatives (*IV*, *V*) it was reversed (see also the discussion on the u.v. spectra).

The spectra of the synthesized compounds revealed further three absorption bands of different intensity belonging to the stretching vibrations of NH of the secondary and primary amino group in the region of 3550—3350 cm^{-1} (Fig. 1*b*, *d*).



Scheme 3

The band positions indicated that the conjugated system of the unsaturated amino ketones present in the molecule was in the α-form. The absorption band at 3550 cm^{-1} could be attributed to the stretching vibrations of the free amino group (Scheme 3*a*) and that at 3350 cm^{-1} belonged to the associated amino group (Scheme 3*b*). The third absorption band (at 3460 and 3360 cm^{-1}, respectively) was attributed to the stretching vibrations of ν(NH) of the secondary amino group in the selenocarbamide

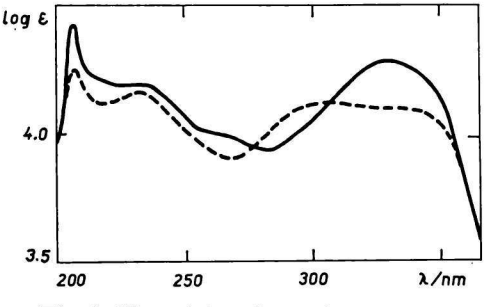


Fig. 2. Ultraviolet absorption spectra.
— α-Acetyl-β-amino(selenocroton)anilide (*IV*); β-amino-α-ethoxycarbonyl(selenocroton)anilide (*I*).

residue on the basis of comparison of the i.r. spectra of the products with the spectra of the appropriate enamines (Table 2).

The u.v. spectra of selenocrotonanilides (*I*—*V*) showed several absorption bands of different intensity in the measured region. Regarding the complexity of the structures of the studied compounds it was difficult to attribute these bands to the appropriate chromophore systems. However, it can be stated that the absorption bands in the 200—260 nm region belonged to the benzenoid chromophore system and the broad band at higher wavenumbers (λ_{max} = 332 nm), considering its position and intensity, corresponded to $\pi \rightarrow \pi^*$ transitional state of the enamine chromophore system (Scheme 2). With the α-ethoxycarbonyl derivatives (*I*—*III*) this band was split into two maxima; it could be explained by the disturbing interference of the ethoxy group in the conjugated enamine system (Fig. 2, Scheme 2, Table 2).

The results of i.r., u.v., and n.m.r. spectra (given in the Experimental) proved unambiguously the structure of 5-(4-chloroanilino)-1,2,3-selenodiazole (*VI*).

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