Reactions of 4-substituted cinnamoyl isothiocyanates with 1-phenoxy-2,3-epoxypropane and sodium hydrogen selenide

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The synthesis of 2-(4-X-cinnamoylimino)-5-phenoxymethyl-1,3-oxathiolanes and 6-(4-X-phenyl)-2-thioxo-4-oxoperhydro-1,3-selenazines by cyclization of 4-substituted cinnamoyl isothiocyanates with 1-phenoxy-2,3-epoxypropane and sodium hydrogen selenide, respectively, is described. The structures of the nine synthesized compounds were proved by i.r. and ^{1}H-n.m.r. spectroscopy.

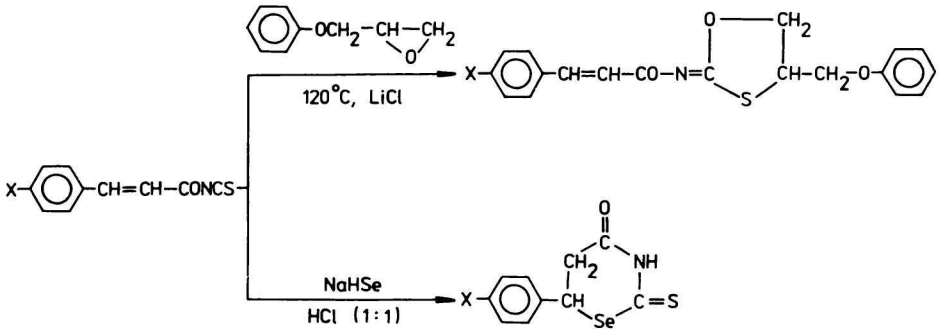
В работе описывается синтез 2-(4-Х-циннамоилимино)-5-феноксиметил-1,3-оксатиоланов и 6-(4-Х-фенил)-2-тиоксо-4-оксопергидро-1,3-селеназинов циклизацией 4-замещенных циннамоилизотиоцианатов с 1-фенокси-2,3-эпоксипропаном или гидроселенидом натрия. Спектры ^{1}Н-ЯМР и ИК подтвердили структуру девяти новосинтезированных соединений.

Addition-cyclization and cycloaddition reactions of acyl isothiocyanates are more and more used for the preparation of new types of heterocyclic compounds, *e.g.* pyrimidines, thiazines, benzoxazines, thiadiazoles, *etc.* [1—5]. *Feinauer* and coworkers [6, 7] dealt with synthesis and properties of 1,3-oxathiolanes prepared from acetyl and benzoyl isothiocyanates. The reactions of sodium hydrogen selenide with different types of isothiocyanates led to preparation of new heterocyclic compounds [8].

On the basis of the mentioned facts we focused our attention on the study of these reactions with 4-substituted cinnamoyl isothiocyanates, which showed high biological activity [9], on purpose to obtain further types of 1,3-oxathiolanes and 1,3-selenazines. 4-Substituted cinnamoyl isothiocyanates as well as 1-phenoxy-2,3-epoxypropane and sodium hydrogen selenide, respectively, were used as starting compounds for the synthesis of 1,3-oxathiolanes and 1,3-selenazines.

The synthesis (Scheme 1) of 1,3-oxathiolanes was carried out by direct heating of 4-substituted cinnamoyl isothiocyanates with 1-phenoxy-2,3-epoxypropane under the catalytic action of lithium chloride at 120°C [6]. Addition of sodium

hydrogen selenide on the 4-substituted cinnamoyl isothiocyanates resulted in unstable addition products which after intramolecular stabilization (due to high nucleophilicity of selenium) afforded 1,3-selenazines.



Scheme 1

Experimental

Cinnamoyl isothiocyanate, 4-methylcinnamoyl isothiocyanate, 4-methoxycinnamoyl isothiocyanate, 4-chlorocinnamoyl isothiocyanate, and 4-bromocinnamoyl isothiocyanate were synthesized from the appropriate 4-substituted cinnamoyl chlorides and lead thiocyanate in benzene [10]. 1-Phenoxy-2,3-epoxypropane was prepared by treatment of 1-chloro-2,3-epoxypropane with phenol in the presence of sodium hydroxide [11] and sodium hydrogen selenide by the reaction of sodium borohydride with selenium in ethanol [12].

Infrared spectra of the synthesized compounds *I*—*X* were measured on a UR 20 spectrophotometer (Zeiss, Jena) in the region of 700—3600 cm^{-1} in chloroform (anal. grade); concentration 0.05 mol l^{-1}.

^{1}H-N.m.r. spectra were measured with a Tesla BS 487 A apparatus at 80 MHz in deuteriochloroform (0.4 mol l^{-1}) using hexamethyldisiloxane as internal standard.

2-(4-X-Cinnamoylimino)-5-phenoxymethyl-1,3-oxathiolanes (I—V)

To the 4-substituted cinnamoyl isothiocyanate (0.01 mol) 1-phenoxy-2,3-epoxypropane (0.01 mol) and lithium chloride (0.0001 mol) were added and the reaction mixture was heated at 120°C for 5 h. Then the mixture was cooled and the solid product was crystallized

Table 1

Characterization of the synthesized compounds

Compound	X	Formula	*M*	Calculated/found			Yield %	M.p., °C Solvent
				% C	% H	% N		
2-(4-X-Cinnamoylimino)-5-phenoxymethyl-1,3-oxathiolanes								
I	H	$C_{19}H_{17}NO_3S$	339.4	67.06 67.27	5.14 5.05	4.24 4.13	44	142—143 Ethanol
II	CH_3	$C_{20}H_{19}NO_3S$	353.4	67.97 67.58	5.42 5.07	3.96 4.12	42	165—167 Ethanol
III	CH_3O	$C_{20}H_{19}NO_4S$	369.5	65.02 64.86	5.18 5.27	3.79 3.65	45	155—157 Ethanol
IV	Cl	$C_{19}H_{16}ClNO_3S$	373.9	61.04 60.82	4.31 4.58	3.75 3.83	44	143—144 Ethanol
V	Br	$C_{19}H_{16}BrNO_3S$	418.3	54.55 54.91	3.86 3.44	3.55 2.98	43	149—151 Ethanol

Table 1 (Continued)

Compound	X	Formula	*M*	Calculated/found			Yield	M.p., °C
				% C	% H	% N	%	Solvent
6-(4-X-Phenyl)-2-thioxo-4-oxoperhydro-1,3-selenazines								
VI	H	$C_{10}H_9NOSSe$	270.0	44.46 44.67	3.33 3.51	5.18 5.38	79	132—133 Chloroform—petroleum ether
VII	CH_3	$C_{11}H_{11}NOSSe$	284.2	46.48 46.17	3.90 3.82	4.93 4.96	78	131—132 Ethanol—water
VIII	CH_3O	$C_{11}N_{11}NO_2SSe$	300.2	41.01 41.08	3.69 3.84	4.67 4.45	72	147—149 Ethanol—water
IX	Cl	$C_{10}H_8ClNOSSe$	318.9	37.69 37.32	2.53 2.81	4.39 4.58	87	154—155 Ethanol—water
X	Br	$C_{10}H_8BrNOSSe$	349.1	34.40 34.53	2.31 2.45	4.01 3.86	86	146—148 Ethanol—water

Table 2

Infrared (cm^{-1}) and ^1H-n.m.r. (p.p.m.) spectral data of the synthesized compounds

Compound	γ(CH=CH)	ν(C=C)	ν(C=O)	ν(NH)	ν(NHCS)	δCH₃	δCH₂	δCH	δCH=CH	δC₆H₅	J_{AB}, Hz
I	982	1619	1543; 1643	—	—	—	3.56; 4.27	5.11	6.65; 7.85	7.25	16
II	987	1621	1553; 1646	—	—	2.32	3.97; 4.27	5.05	6.62; 7.85	7.15	16
III	985	1616	1552; 1644	—	—	3.62	3.84; 4.27	5.08	6.64; 7.85	7.20	16
IV	986	1615	1540; 1647	—	—	—	3.50; 4.27	5.10	6.65; 7.82	7.20	16
V	984	1616	1540; 1644	—	—	—	3.50; 4.27	5.15	6.65; 7.80	7.20	16
VI	—	—	1721	3345	1060; 1260; 1427	—	3.82	4.63	—	7.33	—
VII	—	—	1722	3339	1055; 1265; 1432	2.32	3.26	4.60	—	7.17	—
VIII	—	—	1723	3341	1064; 1261; 1430	3.77	3.22	4.70	—	7.15	—
IX	—	—	1724	3335	1067; 1266; 1431	—	3.25	4.75	—	7.30	—
X	—	—	1723	3338	1078; 1262; 1430	—	3.25	4.62	—	7.37	—

from ethanol. Characterization of the synthesized compounds and their i.r. and ^{1}H-n.m.r. spectral data are given in Tables 1 and 2.

6-(4-X-Phenyl)-2-thioxo-4-oxoperhydro-1,3-selenazines (VI—X)

To the solution of sodium hydrogen selenide (0.015 mol) 4-substituted cinnamoyl isothiocyanate (0.01 mol) was added in small portions under stirring and cooling. Addition of diluted (1 : 1) hydrochloric acid resulted in the formation of a precipitate which was sucked, washed with water, dried, and crystallized from a suitable solvent. Characterization of the synthesized compounds and their i.r. and ^{1}H-n.m.r. spectral data are given in Tables 1 and 2.

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