Thermal Behaviour of Esters and Nitriles of 2-(3-Acylselenoureido)benzoic and 2-(3-Acylselenoureido)thiophene-3-carboxylic Acids

J. ŠIBOR and P. PAZDERA

Department of Organic Chemistry, Faculty of Science, Masaryk University, CZ-611 37 Brno
e-mail: pazdera@chemi.muni.cz

Received 29 June 1999

Dedicated to Professor Milan Kratochvíl in honour of his 75th birthday

The thermally initiated transformation of esters and nitriles of 2-(3-acylselenoureido)benzoic and 2-(3-acylselenoureido)thiophene-3-carboxylic acids under heating without solvent to the temperature *ca.* 300 °C was studied. The thermal behaviour was studied by methods of the thermal analysis. It was found that selenoureas in ester series afford isoselenoureas at the temperature lower than their melting points. This change occurs in the solid state as an exothermic process. The next exothermic change starts by the following increase in temperature. Two molecules of isoselenoureas eliminate one hydrogen molecule by air oxygen action. The oxidation is connected with Se—Se bond formation and diselenides are formed. Nitriles undergo a transformation to di(2-pyrimidyl)diselenides in the course of several steps in melt in the presence of air oxygen.

The thermally initiated transformation of esters and nitriles of 2-(3-acylselenoureido)benzoic and 2-(3-acylselenoureido)thiophene-3-carboxylic acids *I*—*XVIII* under heating without solvent to the temperature *ca.* 300 °C was studied [1]. The title compounds *I*—*VI* (ester series) [2] and *XIII*—*XVIII* (nitrile series) [3] were synthesized by an addition of corresponding aminoesters or aminonitriles to benzoyl or pivaloyl isoselenocyanates in an acetone solution (Scheme 1). Acylisoselenocyanates were prepared *in situ* by the reaction of acyl chlorides with potassium selenocyanate in anhydrous acetone solutions [4].

The isomerization was observed [2] during the synthesis of compounds *I*—*VI* (ester series) (Scheme 2). The products of this isomerization are isoselenoureas *VII*—*XII*. The isomerization proceeds either by UV irradiation (340—400 nm), or in case of benzoyl derivatives, by treatment with acetic acid. On the other hand, the acid action in the pivaloyl set inhibited this isomerization and evoked the retroisomerization reaction of isoselenourea. The cyano analogues *XIII*—*XVIII* do not yield the isomerization product.

Compounds *I*—*XVIII* show nondestruction changes in the presence of air oxygen during the measurements of melting point. These changes were observed as new types of crystals formations after the sample melted. In the case of selenoureas of the ester series, the changes were observed also before the melting temperature as a change of crystal structure in the solid state.

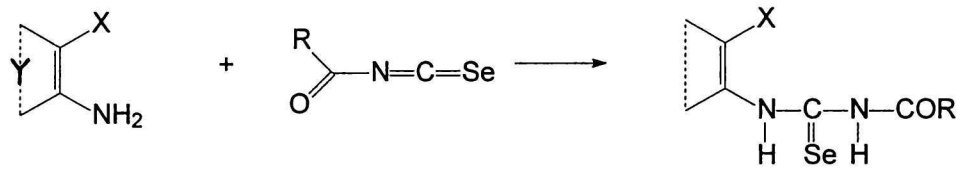
The goal of the presented work is the study of thermal behaviour of esters and nitriles of 2-(3-acylselenoureido)benzoic and -thiophene-3-carboxylic acids *I*—*VI* and *XIII*—*XVIII* and esters of 2-(3-acylisoselenoureido)benzoic and -thiophene-3-carboxylic acids *VII*—*XII* by the methods of thermal analysis.

EXPERIMENTAL

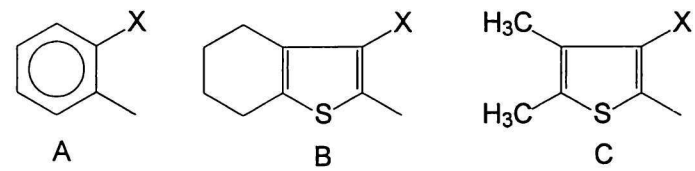
Melting points were measured on Boetius Rapido PHMK 79/2106 (Wägetechnik) instrument. The purity of compounds was tested by elemental analysis on an instrument 1102 (Erba), and by determinations of selenium on spectrometer ICP AES 7500 (Unicam).

The thermal behaviour of compounds was followed with Derivatograph OD-102 (MOM, Budapest). The analyses were provided in about 100 mg samples in a platinum crucible without lid in a stationary atmosphere of the furnace, as a standard material preglowed α-Al_2O_3 was used. The measurements were carried out at 600 °C, TG 100 mg, DTG 1/10, and DTA 1/5. The heating rate was 6 °C min^{-1}.

FTIR spectra were taken on a spectrometer Genesis (Unicam) in potassium bromide pellets. NMR spectra were measured on a Bruker Avance DRX-500 spec-

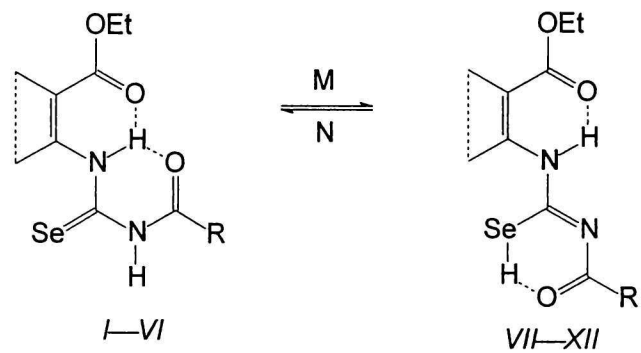


I—VI and *XIII—XVIII*



	Y	R	X		Y	R	X
I	A	Ph	COOEt	*XIII*	A	Ph	CN
II	B	Ph	COOEt	*XIV*	B	Ph	CN
III	C	Ph	COOEt	*XV*	C	Ph	CN
IV	A	*tert*-Bu	COOEt	*XVI*	A	*tert*-Bu	CN
V	B	*tert*-Bu	COOEt	*XVII*	B	*tert*-Bu	CN
VI	C	*tert* Bu	COOEt	*XVIII*	C	*tert* Bu	CN

Scheme 1



I—VI *VII—XII*

	Y	R
I, VII	A	Ph
II, VIII	B	Ph
III, IX	C	Ph
IV, X	A	*tert*-Bu
V, XI	B	*tert*-Bu
VI, XII	C	*tert*-Bu

Isomerization conditions:

M: 1. irradiation by light in methanol solution or on TLC plate
2. controlled heating (80—100 °C)
3. boiling HOAc for R = Ph

N: boiling HOAc for R = *tert*-Bu

Scheme 2

trometer. The ^{13}C and ^{1}H spectra were referenced to tetramethylsilane used as an internal standard or to the solvent signals of $CDCl_3$ and of residual $CHCl_3$ at $\delta = 77.00$ ^{13}C and 7.27 ^{1}H, respectively. Spectral width: 9000 Hz for ^{1}H and 27500 Hz for ^{13}C.

Starting compounds *I—VI* were prepared as in the previous papers [2, 3], acylisoselenoureas *VII—XII* according to [1, 2] and nitriles *XIII—XVIII* according to [3].

Compounds *XIX—XXIV*

Acylselenoureas *I—VI* (0.5 mmol) or acylisoselenoureas *VII—XII* (0.5 mmol) were heated on a microscope slide. The slide was placed on the hot-stage of a melting point apparatus. The samples *I—VI* were heated at temperature of the second exothermic peak on DTA curve ($\theta^{R}_{DTA} \pm 5$ °C) for 10—15 min. The melting temperature of compounds *VII—XII* (exothermic

peak on DTA curve) is identical to that of the compounds *I*—*VI*.

During examination the change and new crystals formation was observed. After cooling to room temperature the crude products *XIX*—*XXIV* were suspended in chloroform. The extract was repeatedly filtered with silica gel and evaporated.

Ethyl 2-{[(Benzoylimino)(2-{(benzoylimino)[2-(ethoxycarbonyl)anilino]methyl}diselenanyl)methyl]amino}benzoate (*XIX*), yield = 0.3 g (81 %), m.p. = 199—207 °C (decomp.). For $C_{34}H_{30}N_4O_6Se_2$ (M_r = 748.5) w_i(calc.): 54.55 % C, 4.04 % H, 9.39 % N, 21.08 % Se; w_i(found): 53.98 % C, 4.12 % H, 9.16 % N, 20.86 % Se. FTIR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 3282, 3179 (NH), 1711, 1245 (COOC), 1655 (NCO), 1625 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ: 1.41 (t, 6H, 2 × OCH_2CH_3, J = 7.0 Hz), 4.18 (q, 4H, 2 × OCH_2CH_3, J = 7.0 Hz), 7.17—8.32 (m, 18H, H_{arom}), 10.86 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 14.34 (CH_3, OCH_2CH_3), 61.28 (CH_2, OCH_2CH_3), 114.28 (C, $CCOOCH_2CH_3$), 118.42 (CH), 119.04 (CH), 122.25 (CH), 128.32 (CH), 128.42 (2 × CH), 129.67 (2 × CH), 131.06 (CH), 136.18 (C), 145.26 (C—Se), 146.28 (C), 169.46 (C=O, $COOCH_2CH_3$), 183.02 (C=O, COC_5H_6).

Ethyl 2-{[(Benzoylimino)(2-{(benzoylimino)[3-(ethoxycarbonyl)-4,5,6,7-tetrahydrobenzo[1]thiophen-2-yl]amino]methyl}diselenanyl)methyl]amino}-4,5,6,7-tetrahydrobenzo[1]thiophene-3-carboxylate (*XX*), yield = 0.35 g (81 %), m.p. = 237—242 °C (decomp.). For $C_{38}H_{38}N_4O_6S_2Se_2$ (M_r = 868.8) w_i(calc.): 52.53 % C, 4.41 % H, 6.45 % N, 18.18 % Se; w_i(found): 51.96 % C, 4.37 % H, 6.51 % N, 18.45 % Se. FTIR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 3271, 3108 (NH), 1728, 1253 (COOC), 1658 (NCO), 1625 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ: 1.45 (t, 6H, 2 × OCH_2CH_3, J = 7.0 Hz), 1.78—2.85 (m, 16H, 2 × C_4H_8), 4.43 (q, 4H, 2 × OCH_2CH_3, J = 7.0 Hz), 7.82—8.37 (m, 10H, H_{arom}), 10.86 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 14.25 (CH_3, OCH_2CH_3), 22.65 (CH_2), 22.87 (CH_2), 24.48 (CH_2), 27.12 (CH_2), 63.84 (CH_2, OCH_2CH_3), 118.32 (C, $CCOOCH_2CH_3$), 128.28 (2 × CH), 128.96 (C), 131.05 (2 × CH), 131.85 (C), 132.15 (CH), 147.15 (C), 150.84 (C—Se), 166.29 (C=O, $COOCH_2CH_3$), 181.23 (C=O, COC_5H_6).

Ethyl 2-{[(Benzoylimino)(2-{(benzoylimino)[3-(ethoxycarbonyl)-4,5-dimethyl-2-thienylamino]methyl}diselenanyl)methyl]amino}-4,5-dimethyl-3-thiophenecarboxylate (*XXI*), yield = 0.3 g (73 %), m.p. = 226—230 °C (decomp.). For $C_{34}H_{34}N_4O_6S_2Se_2$ (M_r = 816.7) w_i(calc.): 50.00 % C, 4.20 % H, 6.86 % N, 19.34 % Se; w_i(found): 50.28 % C, 4.17 % H, 6.87 % N, 19.86 % Se. FTIR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 3298, 3135 (NH), 1721, 1236 (COOC), 1658 (NCO), 1631 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ: 1.18 (t, 6H, 2 × OCH_2CH_3, J = 7.0 Hz), 2.12 (s, 6H, 2 × CH_3, C-4—thiophene), 2.38 (s, 6H, 2 × CH_3, C-5—thiophene), 3.96 (q, 4H, 2 × OCH_2CH_3, J = 7.0 Hz), 7.65—8.46 (m, 10H, H_{arom}), 11.15 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 12.62 (CH_3, C-4—thiophene), 14.25 (CH_3, OCH_2CH_3), 14.89 (CH_3, C-5—thiophene), 64.12 (CH_2, OCH_2CH_3), 118.60 (C, $CCOOCH_2CH_3$), 126.14 (C, C-4—thiophene), 128.68 (2 × CH), 129.10 (C, C-5—thiophene), 131.07 (2 × CH), 132.74 (CH), 136.29 (C), 147.56 (C, C-2—thiophene), 151.12 (C—Se), 168.24 (C=O, $COOCH_2CH_3$), 179.29 (C=O, COC_5H_6).

Ethyl 2-{[[(2,2-Dimethylpropanoyl)imino](2-{[(2,2-dimethylpropanoyl)imino][2-(ethoxycarbonyl)anilino]methyl}diselenanyl)methyl]amino}benzoate (*XXII*), yield = 0.25 g (71 %), m.p. = 209—212 °C (decomp.). For $C_{30}H_{38}N_4O_6Se_2$ (M_r = 708.6) w_i(calc.): 50.58 % C, 5.41 % H, 7.91 % N, 22.29 % Se; w_i(found): 51.12 % C, 5.36 % H, 8.06 % N, 21.96 % Se. FTIR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 3316, 3124 (NH), 1722, 1250 (COOC), 1661 (NCO), 1623 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ: 1.22 (s, 18H, 2 × $C(CH_3)_3$), 1.42 (t, 6H, 2 × OCH_2CH_3, J = 7.0 Hz), 4.51 (q, 4H, 2 × OCH_2CH_3, J = 7.0 Hz), 7.14—7.52 (m, 8H, H_{arom}), 9.65 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 14.13 (CH_3, OCH_2CH_3), 27.56 (C, $C(CH_3)_3$), 41.32 (CH_3, $C(CH_3)_3$), 60.60 (CH_2, OCH_2CH_3), 113.84 (C, $CCOOCH_2CH_3$), 118.56 (CH), 119.14 (CH), 123.15 (CH), 127.88 (CH), 136.22 (C), 148.52 (C), 151.63 (C—Se), 168.59 (C=O, $COOCH_2CH_3$), 189.67 (C=O, $COC(CH_3)_3$).

Ethyl 2-{[[(2,2-Dimethylpropanoyl)imino](2-{[(2,2-dimethylpropanoyl)imino][3-(ethoxycarbonyl)-4,5,6,7-tetrahydrobenzo[1]thiophen-2-yl]amino]methyl}diselenanyl)methyl]amino}-4,5,6,7-tetrahydrobenzo[1]thiophene-3-carboxylate (*XXIII*), yield = 0.3 g (73 %), m.p. = 227—233 °C (decomp.). For $C_{34}H_{46}N_4O_6S_2Se_2$ (M_r = 828.8) w_i(calc.): 49.27 % C, 5.59 % H, 6.76 % N, 19.05 % Se; w_i(found): 49.07 % C, 5.42 % H, 6.30 % N, 19.12 % Se. FTIR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 3243, 3183 (NH), 1716, 1246 (COOC), 1664 (NCO), 1625 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ: 1.21 (s, 18H, 2 × $C(CH_3)_3$), 1.41 (t, 6H, 2 × OCH_2CH_3, J = 7.0 Hz), 1.76—2.59 (m, 16H, 2 × C_4H_8), 4.40 (q, 4H, 2 × OCH_2CH_3, J = 7.0 Hz), 11.57 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 14.47 (CH_3, OCH_2CH_3), 22.66 (CH_2), 23.02 (CH_2), 24.82 (CH_2), 26.15 (CH_2), 27.61 (CH_3, $C(CH_3)_3$), 42.15 (C, $C(CH_3)_3$), 60.48 (CH_2, OCH_2CH_3), 114.02 (C, $CCOOCH_2CH_3$), 128.02 (C), 132.66 (C), 147.26 (C), 147.53 (C—Se), 166.12 (C=O, $COOCH_2CH_3$), 190.87 (C=O, $COC(CH_3)_3$).

Ethyl 2-{[[(2,2-Dimethylpropanoyl)imino](2-{[(2,2-dimethylpropanoyl)imino][3-(ethoxycarbonyl)-4,5-dimethyl-2-thienylamino]methyl}diselenanyl)methyl]amino}-4,5-dimethyl-3-thiophenecarboxylate (*XXIV*), yield = 0.25 g (64 %), m.p. = 218—226 °C (decomp.). For $C_{30}H_{42}N_4O_6S_2Se_2$ (M_r = 776.7) w_i(calc.): 46.39 % C, 5.45 % H, 7.21 % N, 20.33 % Se; w_i(found): 46.49 % C, 5.37 % H, 7.36 % N, 20.13 % Se.

FTIR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 3314, 3092 (NH), 1728, 1252 (COOC), 1658 (NCO), 1625 (C=N). ^1H NMR spectrum ($CDCl_3$), δ: 1.22 (s, 18H, $C(CH_3)_3$), 1.43 (t, 6H, 2 × OCH_2CH_3, J = 7.0 Hz), 2.15 (s, 6H, 2 × CH_3, C-4—thiophene), 2.39 (s, 6H, 2 × CH_3, C-5—thiophene), 4.36 (q, 4H, 2 × OCH_2CH_3, J = 7.0 Hz), 11.02 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 12.85 (CH_3, C-4—thiophene), 14.66 (CH_3, OCH_2CH_3), 15.03 (CH_3, C-5—thiophene), 27.60 (CH_3, $C(CH_3)_3$), 42.29 (C, $C(CH_3)_3$), 60.50 (CH_2, OCH_2CH_3), 114.78 (C, $CCOOCH_2CH_3$), 129.62 (C, C-4—thiophene), 133.18 (C, C-5—thiophene), 146.56 (C, C-2—thiophene), 146.94 (C—Se), 164.82 (C=O, $COOCH_2CH_3$), 191.06 (C=O, $COC(CH_3)_3$).

Compounds *XXV—XXX*

Acylselenoureas *XIII—XVIII* (0.5 mmol) were heated on a microscope slide. The slide was placed on the hot-stage of a melting point apparatus. The samples *XIII—XVIII* were heated at temperature of the exothermic peak on DTA curve (θ^R_{DTA} ± 5 °C) for 10—15 min.

During examination the change and new crystals formation was observed. After cooling to room temperature the crude products *XXV—XXX* were suspended in chloroform. The extract was repeatedly filtered with silica gel and evaporated.

N-[2-{2-[4-(Benzoylamino)quinazolin-2-yl]diselenanyl}-4-quinazolinyl]benzamide (*XXV*), yield = 0.2 g (61 %), m.p. = 191—196 °C (decomp.). For $C_{30}H_{20}N_6O_2Se_2$ (M_r = 654.4) w_i(calc.): 55.06 % C, 3.08 % H, 12.84 % N, 24.13 % Se; w_i(found): 50.28 % C, 3.42 % H, 12.85 % N, 23.96 % Se. FTIR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 1729 (C=O). ^1H NMR spectrum ($CDCl_3$), δ: 7.56—8.78 (m, 18H, H_{arom}), 9.56 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 123.26 (CH), 126.28 (CH), 126.68 (CH), 126.72 (CH), 127.82 (CH), 129.84 (CH), 129.96 (CH), 130.16 (CH), 131.12 (CH), 138.62 (C), 141.82 (C) 143.12 (C), 150.20 (C—Se), 162.18 (C), 169.24 (C=O).

N-[2-{2-[4-(Benzoylamino)-5,6,7,8-tetrahydrobenzo-[4,5]thieno[2,3-d]pyrimidin-2-yl]diselenanyl}-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-4-yl]benzamide (*XXVI*), yield = 0.3 g (77 %), m.p. = 232—236 °C (decomp.). For $C_{34}H_{28}N_6O_2S_2Se_2$ (M_r = 774.7) w_i(calc.): 52.71 % C, 3.64 % H, 10.85 % N, 20.39 % Se; w_i(found): 52.53 % C, 3.41 % H, 10.45 % N, 20.18 % Se. FTIR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 1738 (C=O). ^1H NMR spectrum ($CDCl_3$), δ: 1.45—2.58 (m, 16H, 2 × C_4H_8), 7.56—7.94 (m, 10H, H_{arom}), 9.16 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 22.54 (CH_2), 22.79 (CH_2), 23.96 (CH_2), 24.58 (CH_2), 127.24 (2 × CH), 128.05 (2 × CH), 129.15 (C), 131.26 (C), 132.38 (CH), 135.14 (C), 146.16 (C), 149.36 (C), 151.26 (C—Se), 163.18 (C), 168.24 (C=O).

N-[2-{2-[4-(Benzoylamino)-5,6-dimethylthieno-[2,3-d]pyrimidin-2-yl]diselenanyl}-5,6-dimethylthieno-[2,3-d]pyrimidin-4-yl]benzamide (*XXVII*), yield = 0.2 g (55 %), m.p. = 214—219 °C (decomp.). For $C_{30}H_{24}N_6O_2S_2Se_2$ (M_r = 722.6) w_i(calc.): 49.86 % C, 3.35 % H, 11.63 % N, 21.85 % Se; w_i(found): 50.06 % C, 3.41 % H, 11.78 % N, 21.42 % Se. FTIR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 1736 (C=O). ^1H NMR spectrum ($CDCl_3$), δ: 2.32 (s, 6H, 2 × CH_3, C-4—thiophene), 2.54 (s, 6H, 2 × CH_3, C-5—thiophene), 7.12—7.84 (m, 10H, H_{arom}), 9.14 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 12.62 (CH_3, C-4—thiophene), 14.37 (CH_3, C-5—thiophene), 126.93 (C, C-4—thiophene), 127.89 (2 × CH), 129.26 (C, C-5—thiophene), 130.16 (2 × CH), 131.64 (CH), 134.26 (C), 136.18 (C), 144.95 (C, C-2—thiophene), 150.89 (C—Se), 164.12 (C), 169.26 (C=O).

N-[2-(2-{4-[(2,2-Dimethylpropanoyl)amino]-2-quinazolinyl}diselenanyl)-4-quinazolinyl]-2,2-dimethylpropanamide (*XXVIII*), yield = 0.2 g (65 %), m.p. = 190—193 °C (decomp.). For $C_{26}H_{28}N_6O_2Se_2$ (M_r = 614.5) w_i(calc.): 50.82 % C, 4.59 % H, 13.68 % N, 25.70 % Se; w_i(found): 50.58 % C, 4.41 % H, 13.19 % N, 25.29 % Se. FTIR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 1736 (C=O). ^1H NMR spectrum ($CDCl_3$), δ: 1.12 (s, 18H, 2 × $C(CH_3)_3$), 7.16—7.96 (m, 8H, H_{arom}), 9.54 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 27.60 (C, $C(CH_3)_3$), 42.22 (CH_3, $C(CH_3)_3$), 118.82 (CH), 119.24 (CH), 123.60 (CH), 128.05 (CH), 136.16 (C), 146.24 (C), 149.27 (C—Se), 161.18 (C), 168.59 (C=O).

N-[2-(2-{4-[(2,2-Dimethylpropanoyl)amino]-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidin-2-yl}diselenanyl)-5,6,7,8-tetrahydrobenzo[4,5]thieno-[2,3-d]pyrimidin-4-yl]-2,2-dimethylpropanamide (*XXIX*), yield = 0.3 g (81 %), m.p. = 233—238 °C (decomp.). For $C_{30}H_{36}N_6O_2S_2Se_2$ (M_r = 734.7) w_i(calc.): 49.04 % C, 4.34 % H, 11.44 % N, 21.94 % Se; w_i(found): 49.21 % C, 4.54 % H, 11.76 % N, 21.05 % Se. FTIR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 1725 (C=O). ^1H NMR spectrum ($CDCl_3$), δ: 1.22 (s, 18H, 2 × $C(CH_3)_3$), 1.45—2.56 (m, 16H, 2 × C_4H_8), 9.16 (s, 2H, 2 × NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 22.56 (CH_2), 22.68 (CH_2), 23.17 (CH_2), 24.42 (CH_2), 27.60 (CH_3, $C(CH_3)_3$), 42.21 (C, $C(CH_3)_3$), 132.49 (C), 134.74 (C), 147.05 (C), 149.27 (C), 151.32 (C—Se), 164.18 (C), 171.26 (C=O).

N-[2-(2-{4-[(2,2-Dimethylpropanoyl)amino]-5,6-dimethylthieno[2,3-d]pyrimidin-2-yl}diselenanyl)-5,6-dimethylthieno[2,3-d]pyrimidin-4-yl]-2,2-dimethylpropanamide (*XXX*), yield = 0.2 g (65 %), m.p. = 220—224 °C (decomp.). For $C_{26}H_{32}N_6O_2S_2Se_2$ (M_r = 682.6) w_i(calc.): 45.75 % C, 4.73 % H, 12.31 % N, 23.13 % Se; w_i(found): 45.39 % C, 4.36 % H, 12.21 % N, 22.94 % Se. FTIR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 1725 (C=N). ^1H NMR spectrum ($CDCl_3$), δ: 1.22 (s, 18H, $C(CH_3)_3$), 2.32 (s, 6H, 2 × CH_3, C-4—thiophene), 2.53 (s, 6H, 2 × CH_3, C-5—thiophene), 9.18 (s, 2H, 2

Table 1. Temperature Values of Exothermic $\theta^{E}_{1,2}$ and Endothermic $\theta^{M}_{1,2}$ Peaks of Compounds *I*—*XII* and *XIX*—*XXIV* and their Melting Points

Compounds	θ^{E}_{1}/°C	θ^{M}_{1}/°C	M.p./°C	θ^{E}_{2}/°C	θ^{M}_{2}/°C	M.p.*/°C
I, XIX	89	110	107—110	152	207	195—207
VII, XIX	–	110	107—110	152	207	195—207
II, XX	152	173	172—174	194	242	237—242
VIII, XX	–	173	173—174	194	242	237—242
III, XXI	163	174	173—175	185	230	226—230
IX, XXI	–	174	175—178	185	230	226—230
IV, XXII	89	111	109—112	158	212	209—212
X, XXII	–	111	110—112	158	212	209—212
V, XXIII	144	154	153—155	181	233	227—233
XI, XXIII	–	154	156	181	233	227—233
VI, XXIV	150	185	183—186	196	226	218—226
XII, XXIV	–	185	185—187	196	226	218—226

*Decomposition.

× NH). ^{13}C NMR spectrum ($CDCl_3$), δ: 12.60 (CH_3, C-4—thiophene), 14.39 (CH_3, C-5—thiophene), 27.60 (CH_3, $C(CH_3)_3$), 42.20 (C, $C(CH_3)_3$), 129.94 (C, C-4—thiophene), 131.85 (C, C-5—thiophene), 148.16 (C, C-2—thiophene), 149.64 (C), 151.05 (C—Se), 164.27 (C), 170.02 (C=O).

DISCUSSION

Esters of 2-(3-acylselenoureido)benzoic and -thiophene-3-carboxylic acids *I*—*VI*, the same as esters of 2-(3-acylisoselenoureido)benzoic and -thiophene-3-carboxylic acids *VII*—*XII* were prepared following paper [2] (Schemes 1 and 2).

We have observed the identical melting points for the corresponding pairs of compounds during melting point measurements of the compounds *I*—*VI* and their isomers *VII*—*XII*. We have also found that changes proceeded at temperature lower than their melting point in the "solid state" in the case of *I*—*VI*. These changes of crystalline structure proceeded without melting of starting crystals. The compounds *VII*—*XII* did not exhibit these changes. Both types of compounds (*I*—*VI* and *VII*—*XII*) exhibited further changes when temperature raised beyond melting point. This macroscopic observation was very interesting for us and we have studied these changes by the thermal analysis method.

Thermal analyses of compounds *I*—*VI* showed two exothermic θ^{E} and two endothermic θ^{M} peaks on DTA curve. On the other hand, acylisoselenoureas *VII*—*XII* exhibited only endothermic peaks (first pair of peaks *I*—*VI*) and the second peak was the same as in the compounds *I*—*VI* (Table 1 and Fig. 1).

We assume that the exothermic process (θ^{E}_{1} peaks on DTA curve of *I*—*VI*) is connected with the isomerization of the starting selenoureas *I*—*VI* and with a reorganization of the crystalline sample. The character of TG and DTG curves supports this assumption. The shape of both curves is in the above-mentioned

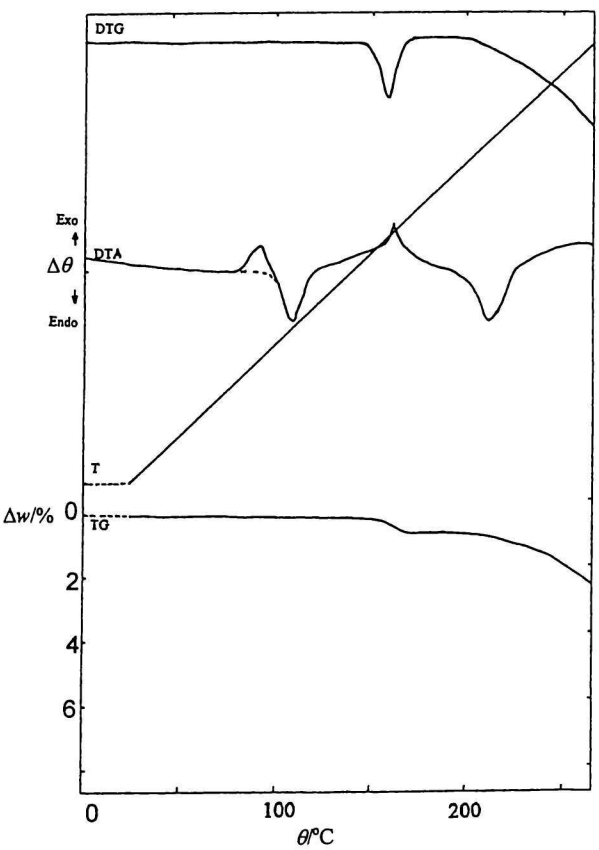
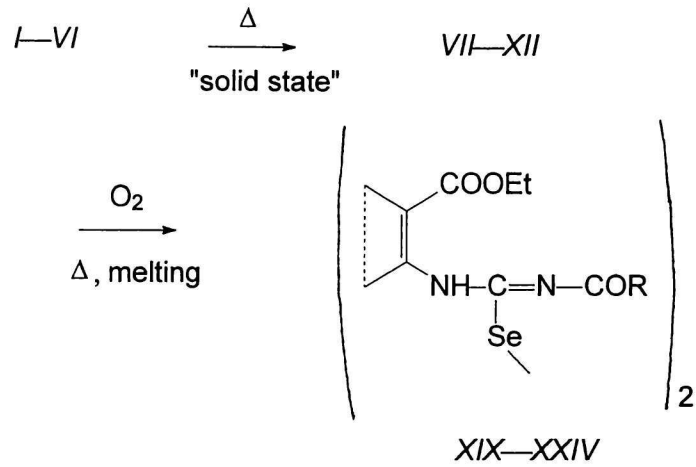


Fig. 1. TG, DTG, and DTA curves of compounds, *I*, *VII*, and *XIX*.

range without changes of mass and isomerization proceeds in the solid sample without melting. We have suggested that the isomerization of acylselenoureas *I*—*VI* to acylisoselenoureas *VII*—*XII* in the "solid state" proceeded for the reason of favourable crystal structure arrangement. The interatomic distance of two molecules on the structure fragment CONH—SeC (0.31 nm) was found for compounds *V* by X-ray anal-



	Y	R		Y	R
I, VII, XIX	A	Ph	*IV, X, XXII*	A	*tert*-Bu
III, VIII, XX	B	Ph	*V, XI, XXIII*	B	*tert*-Bu
III, IX, XXI	C	Ph	*VI, XII, XXIV*	C	*tert*-Bu

Scheme 3

Table 2. Temperature Values of Exothermic $\theta^{E}_{1,2}$ and Endothermic $\theta^{M}_{1,2}$ Peaks of Compounds *XIII—XVIII* and *XXV—XXX* and their Melting Points

Compounds	θ^{E}_{1}/°C	θ^{M}_{1}/°C	M.p./°C	θ^{E}_{2}/°C	θ^{M}_{2}/°C	M.p.*/°C
XIII, XXV	–	154	153—155	162	195	191—196
XIV, XXVI	–	202	201—204	221	236	232—236
XV, XXVII	–	114	112—115	165	219	214—219
XVI, XXVIII	–	147	146—148	159	190	190—193
XVII, XXIX	–	179	178—180	201	236	233—238
XVIII, XXX	–	163	163—165	177	224	220—224

*) Decomposition

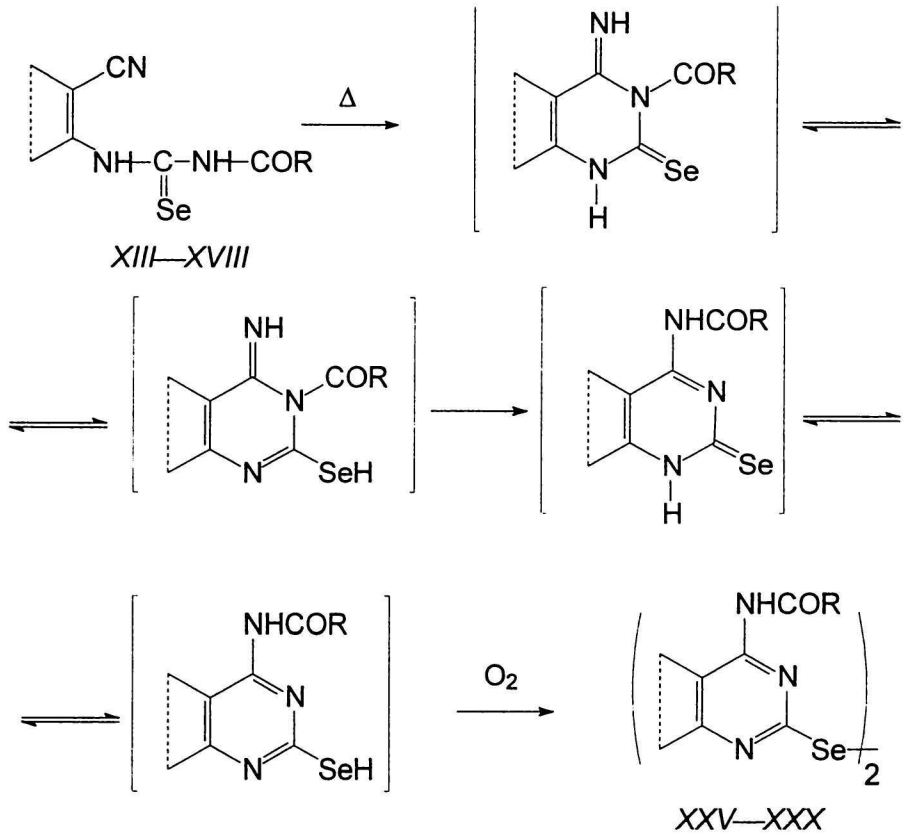
ysis [2]. It is possible to presume that the prolongation of corresponding bonds was caused (for the reason of vibration raising) by the heating (energy supply). The following step is intermolecular transfer of hydrogen from nitrogen atom of acylamino group to selenium of the second molecule. The mentioned presumption is also distinctly apparent from the ORTEP picture of compound *V* [2]. The endothermic peak θ^{M}_{1} on the DTA curve corresponds to the melting point.

The second pair of peaks is identical for both types of compounds (*I—VI* and *VII—XII*) because only acylisoselenoureas *VII—XII* are presented in the reaction mixture. The acylselenoureas *I—VI* lead to acylisoselenoureas *VII—XII* by heating at temperature lower than their melting point as mentioned above. Further temperature increase (melting point) leads to an exothermic action (θ^{E}_{2} peaks on DTA curve). The macroscopic changes were also observed on the hot-stage microscope. The melts of compounds *VII—XII* solidified at temperature corresponding to the values of θ^{E}_{2} on DTA curve. We have suggested the diselenides *XIX—XXIV* formation (Scheme 3) because one hydrogen molecule is eliminated. This assumption is supported by a mass decrease on the TG curve corresponding to the hydrogen atom. The hydrogen is oxidized to water by air oxygen action. The endothermic peak θ^{M}_{2} on the DTA curve corresponding to the melting point is connected with decomposition of diselenides *XIX—XXIV*.

TLC, C, H, N, Se elemental analysis, FTIR, ^{1}H and ^{13}C NMR spectra showed products *VII—XII* to be identical with acylisoselenoureas [2].

The C, H, N, Se elemental analysis, FTIR, ^{1}H and ^{13}C NMR spectra supported the identification of diselenides *XIX—XXIV*. In the FTIR spectra NHCSe and NHCO vibrational bands were not observed but the NCO and C=N bands were found. The one type of NH proton was found at $\delta \approx 10$. The chemical shift of C—Se was downfield ($\delta \approx 150$).

The thermal analyses of compounds *XIII—XVIII* showed that during temperature raising in all cases a change was found. However, changes were not observed for temperature lower than their melting point. Characteristic records of DTA, DTG, and TG curves



XIII—XVIII

XXV—XXX

	Y	R		Y	R
XIII, XXV	A	Ph	*XVI, XXVIII*	A	*tert*-Bu
XIV, XXVI	B	Ph	*XVII, XXIX*	B	*tert*-Bu
XV, XXVII	C	Ph	*XVIII, XXX*	C	*tert*-Bu

Scheme 4

(Table 2, Fig. 2) showed no changes for this temperature.

Changes were not observed also in hot-stage microscope. The first change was found accompanied by an endothermic peak θ_1^M on the DTA curve. This change corresponded to the temperature of melting point. Further temperature increase led to an exothermic action (exothermic peak θ_2^E on the DTA curve). This exothermic action is connected with a mass decrease (TG and DTG curves). The change of the mass corresponds to half hydrogen molecule. We suggest that starting acylselenoureas *XIII—XVIII* dimerized to di(2-pyrimidylselenides) *XXV—XXX* (Scheme 4). The hydrogen is eliminated and oxidized to water by air oxygen action. The next temperature raising corresponds to endothermic peak on the DTA curve. The temperature corresponding to endothermic peak is the melting point of compounds *XXV—XXX*.

We have suggested that the cycloaddition of acylamino group to carbon of the cyano group is the first reaction step. During this reaction the pyrimidine skeleton was formed. The mentioned presumption is supported by the finding that 3-alkylselenoureidobenzonitriles and 3-acylselenoureidobenzonitriles undergo the thermally initiated cyclization to corresponding quinazoline derivatives [5]. The next temperature increase was followed by 4-R-aminoquinazoline system formation (the Dimroth rearrangement) [5]. We have suggested that the mentioned sequence may be used for thermally initiated transformation of presented nitriles *XIII—XVIII*. The product of Dimroth rearrangement undergoes the oxidation by air under Se—Se bond formation. Intermediates in Scheme 4 (cycloaddition product and product of Dimroth rearrangement) were not observed.

The structures of diselenides *XXV—XXX* were supported by elemental analysis, FTIR, ^{1}H and ^{13}C NMR spectroscopy. In the FTIR spectra corresponding CN and NHCSe bands were not found. On the other hand, very intensive band was observed at about 1730 cm^{-1} and was assigned to the carbonyl group. In the ^{1}H NMR spectra one type of protons was observed at the chemical shift $\delta \approx 9$ (assignment NH). The chemical shift of carbon atom C—Se ($\delta = 150$) is lower than that of C=Se ($\delta \approx 180$).

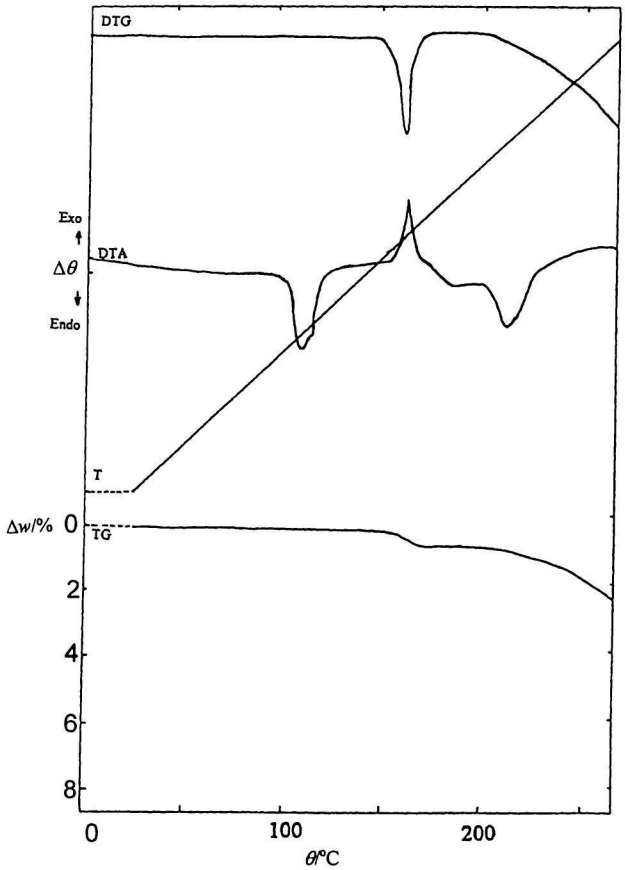


Fig. 2. TG, DTG, and DTA curves of compounds *XV* and *XXVII*.

Acknowledgements. This work was supported by the Grant No. 203/93/0715 of the Grant Agency of the Czech Republic and by the Grant of Ministry of Education (CEZ:J07/98: 143100011). The authors thank Dr. J. Jambor of the Department of Analytical Chemistry of their Faculty for determination of selenium by ICP AES, Analytical Department of Lachema, Brno, Czech Republic for elemental analysis, and Advanced Chemistry Development, Inc., Toronto, Canada for the free on-line simulation of ^{1}H *and* ^{13}C *NMR spectra.*

REFERENCES

1. Šibor, J. and Pazdera, P., *Chem. Listy 91* (9), 675 (1997).
2. Pazdera, P., Šibor, J., Marek, R., Kutý, M., and Marek, J., *Molecules 2*, 135 (1997).
3. Šibor, J., Žůrek, D., Marek, R., Kutý, M., Marek, J., and Pazdera, P., *Collect. Czech. Chem. Commun. 10*, 1673 (1999).
4. Douglas, I. B., *J. Am. Chem. Soc. 59*, 740 (1937).
5. Havránek, M. and Pazdera, P., unpublished results.