FUSION REACTIONS OF *N*-HETEROCYCLIC MOIETIES TO THIOPYRANO[4′,3′:4,5]THIENO[2,3-*d*]PYRIMIDINES

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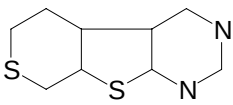
Dedicated to Professor K. Gewald, TU Dresden, on the occasion of his 65th birthday.

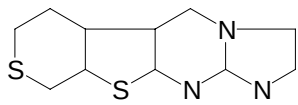
Derivatives of the novel heterocyclic parent systems imidazolo[1,2-*a*]thiopyrano[4′,3′:4,5]thieno[2,3-*d*]-pyrimidine (*B*) and thiopyrano[4′,3′:4,5]thieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine (*C*) have been synthesized by fusing pyrimidine moieties to 2-amino-4,7-dihydro-5*H*-thieno[2,3-*c*]thiopyran-3-carboxylic acid ethyl ester (**1**) and -3-carbonitrile (**10**), followed by cyclization reactions of the title intermediates *A* thus obtained.

Key words: Annelation reactions; Thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidines.

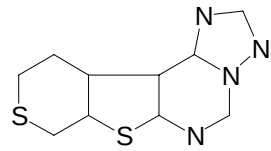
In three papers published recently[1–3] we reported on annelation reactions of pyrimidine moieties at (hetero)aromatic systems, on some ways to synthesize products derived from the thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidine system (*A*) and on various fusion reactions to this system carried out to approach novel tetracyclic systems. The present paper is following that line of research by reporting on a new series of linear and angular fusion reactions to this system, in which imidazole and 1,2,4-triazole moieties were annelated, yielding derivatives of the novel tetracyclic ring systems *B* and *C*.



A



B



C

An approach to system *B* started from 2-amino-4,7-dihydro-5*H*-thieno[2,3-*c*]thiopyran-3-carboxylic acid ethyl ester[4] (**1**), which was converted into 5,8-dihydro-2-methylthio-4-oxo-4*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidin-4-one (**7**). On reaction

with hydrazine hydrate the methylthioester **7** yielded the target *N*-aminolactam **9**. As depicted in Scheme 1, the key intermediate **7** can be obtained – in addition to the BMMA-method (utilization of bis(methylthio)methylenamino reagents) which we published recently[1] – by one of the following two sequences: (i) preparation of 2-thioxo-1,5,6,8-tetrahydro-2*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidin-4(3*H*)-one (**5**) according to published procedures[2] (i.e. by reaction with ethoxycarbonylisothiocyanate and ensuing cyclization), followed by *S*-methylation to **6** and *N*-substitution, or (ii) reaction of **1** with ethyl isothiocyanatoacetate to **2**, followed by cyclization to **3** and subsequent methylation.

The desired tetracyclic 1-amino-3,6,7,9-tetrahydro-5*H*-imidazo[1,2-*a*]thiopyrano-[4′,3′:4,5]thieno[2,3-*d*]pyrimidin-2(1*H*),5-dione (**9**) can be obtained either by reaction of the methylthio derivative **7** with hydrazine hydrate (as mentioned above), or alternatively by converting the thioxo-functionality of **3** by $POCl_3$ into the replaceable chloro substituent of **8** and by final cyclization of **8** with hydrazine hydrate.

Approaches to derivatives of parent system *C* were started from 2-amino-4,7-dihydro-5*H*-thieno[2,3-*c*]thiopyran-3-carbonitrile (**10**) obtained according to the literature[5]. The nitrile **10** upon consecutive reactions with orthoformate (leading to **11**) and hydrazine hydrate gave the key intermediate **12** (Scheme 2).

Reactions of compound **12** with ortho esters, trichloroacetonitrile and chloroacetyl chloride according to published methods[6] yielded the compounds **13**, **14** and **15**, respectively, all three of them derived from the new parent system *C*.

EXPERIMENTAL

Melting points were determined on a Kofler melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory, Institute of Physical Chemistry, University of Vienna (Mag. J. Theiner). ^{13}C and ^{1}H NMR spectra (δ, ppm) were measured on a Bruker AC 200 spectrometer (^{1}H at 200.13 MHz, ^{13}C at 50.32 MHz frequency) 5 mm dual $^{1}H/^{13}C$- VT probe head at 300 K; solvent: $(CD_3)_2SO$ and $CDCl_3$, respectively; internal standard TMS. IR spectra ($\tilde{\nu}$, cm^{-1}) were recorded on a Shimadzu 470 Spectrophotometer in KBr pellets.

Ethyl 2-[(Ethoxycarbonylmethylaminothiocarbonyl)amino]-4,7-dihydro-5*H*-thieno[2,3-*c*]thiopyran-3-carboxylate (**2**)

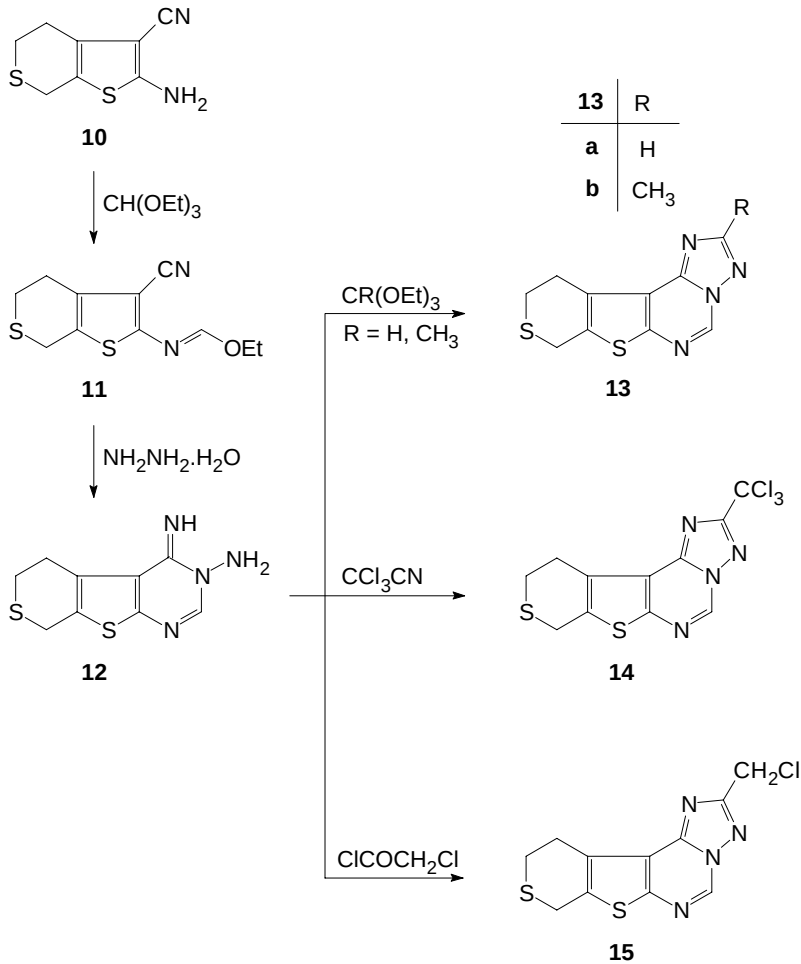
A solution of ethoxycarbonylmethylisothiocyanate (0.73 g, 0.005 mol) was added to a stirred solution of compound **1** (ref.[4], 1.21 g, 0.0049 mol) in absolute ethanol (10 ml). The whole mixture was heated under reflux for 2 h. On cooling, the separated solid product was collected by filtration, dried and recrystallized from ethanol. Yield: 1.6 g (84%) of compound **2** as white crystals, m.p. 163–165 °C. For $C_{15}H_{20}N_2O_4S_3$ (388.5) calculated: 46.36% C, 5.18% H, 7.21 N; found: 46.29% C, 4.97% H, 7.18% N. IR spectrum: 1 500, 1 580, 1 660, 1 720, 2 980, 2 990, 3 100, 3 300. ^{1}H NMR spectrum ($(CD_3)_2SO$): 1.20 t, 3 H ($COOCH_2C\mathbf{H}_3$); 1.30 t, 3 H ($COOCH_2C\mathbf{H}_3$); 2.85 t, 2 H (H-4); 2.95 t, 2 H (H-5); 3.70 s, 2 H (H-7); 4.15 q, 2 H ($COOCH_2CH_3$); 4.20–4.40 m, 4 H ($COOC\mathbf{H}_2CH_3$, CH_2COO); 9.90 s, 1 H (NH); 11.60 s, 1 H (NH). ^{13}C NMR spectrum ($(CD_3)_2SO$): 14.02 q ($COOCH_2\mathbf{C}H_3$), 14.03 q ($COOCH_2\mathbf{C}H_3$), 24.14 t (C-4), 25.43 t (C-5), 27.64 t (C-7), 45.45 t ($NHCH_2$), 60.48 t ($COO\mathbf{C}H_2CH_3$), 60.56 t ($COO\mathbf{C}H_2CH_3$), 111.66 s (C-3), 121.63 s (C-7a), 129.50 s (C-3a), 149.10 s (CO), 165.43 s (CO), 168.99 s (C-2), 178.62 s (C=S).

CO2Et
NHCSNHCH2CO2Et
2
NaOEt
O
N
CO2Et
S
N
H
3
POCl3
Cl
8
SCNCH2CO2Et
1
NH2
CH3I/NaOH
SCH3
7
NH2NH2.H2O
O
N
NH2
9
SCNCO2Et
4
NaOEt
5
CH3I/K2CO3
6
BrCH2CO2Et

SCHEME 1

Ethyl 4-Oxo-2-thioxo-1,5,6,8-tetrahydro-2*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidine-3(4*H*)-acetate (**3**)

Compound **2** (1 g, 0.0025 mol) was dissolved in a solution of sodium ethoxide (from 0.06 g, 0.0025 mol, sodium and 10 ml absolute ethanol) and the solution was stirred at room temperature for 5 min. The sodium salt of compound **3** was collected, then dissolved in water and neutralized (to pH 4) with hydrochloric acid. The separated product was collected by filtration, washed with ethanol, dried and recystallized from ethanol. Yield: 0.75 g (85%) of compound **3** as white crystals, m.p. 238–240 °C. For $C_{13}H_{14}N_2O_3S_3$ (342.4) calculated: 45.59% C, 4.12% H, 8.18% N; found: 44.93% C, 4.03% H, 8.07% N. IR spectrum: 1 400, 1 460, 1 500, 1 640, 1 720, 2 990, 3 000, 3 400. ^{1}H NMR spectrum



SCHEME 2

($(CD_3)_2SO$): 1.20 t, 3 H ($COOCH_2C\mathbf{H}_3$); 2.85 t, 2 H (H-5); 3.00 t, 2 H (H-6); 3.80 s, 2 H (H-8); 4.10 q, 2 H ($COOC\mathbf{H}_2CH_3$); 5.10 s, 2 H (CH_2COO); 13.80 s, 1 H (NH). ^{13}C NMR spectrum ($(CD_3)_2SO$): 14.92 q ($COOCH_2\mathbf{C}H_3$), 24.05 t (C-5), 24.46 t (C-6), 26.91 t (C-8), 60.54 t ($N\mathbf{C}H_2$), 61.73 t ($COO\mathbf{C}H_2CH_3$), 116.63 s (C-4a), 124.02 s (C-4b), 130.61 s (C-8a), 149.51 s (C-9a), 156.95 s (C-4), 173.11 s (C-2), 187.75 (CO ester).

Ethyl 2-[(Ethoxycarbonylaminothiocarbonyl)amino]-4,7-dihydro-5*H*-thieno[2,3-*c*]thiopyrane-3-carboxylate (**4**)

A solution of ethoxycarbonylisothiocyanate (prepared by mixing ethylchloroformate (1.08 g, 0.01 mol) in dry acetone with ammonium thiocyanate (0.76 g, 0.01 mol) and heating in a water bath for 20 min) was added to a stirred solution of compound **1** (2.4 g, 0.01 mol) in acetone (30 ml). The whole mixture was heated under reflux in a water bath for 2 h, then evaporated in vacuo. The remaining product was triturated with ethanol, then collected by filtration, dried and recrystallized from ethanol. Yield: 2.6 g (70%) of compound **4** as yellow crystals, m.p. 175–176 °C. For $C_{14}H_{18}N_2O_4S_3$ (374.5) calculated: 44.89% C, 4.84% H, 7.48% N; found: 45.03% C, 4.56% H, 7.63% N. ^1H NMR spectrum ($CDCl_3$): 1.30 m, 6 H ($2 \times COOCH_2C\mathbf{H}_3$); 2.90 t, 2 H (H-4); 3.20 t, 2 H (H-5); 3.70 s, 2 H (H-7); 4.40 m, 4 H ($2 \times COOC\mathbf{H}_2CH_3$); 8.10 s, 1 H (NH); 14.10 s, 1 H (NH). ^{13}C NMR spectrum ($CDCl_3$): 14.12 q ($OCH_2\mathbf{C}H_3$), 14.22 q ($OCH_2\mathbf{C}H_3$), 25.13 t (C-4), 26.17 t (C-5), 27.92 s (C-7), 60.83 t ($O\mathbf{C}H_2CH_3$), 62.94 t ($O\mathbf{C}H_2CH_3$), 116.16 s (C-3), 123.78 s (C-7a), 131.07 s (C-3a), 146.84 s ($\mathbf{C}OOCH_2CH_3$), 151.21 s ($\mathbf{C}OOCH_2CH_3$), 164.99 s (C-2), 173.39 s (C=S).

2-Thioxo-1,5,6,8-tetrahydro-2*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidin-4(3*H*)-one (**5**)

Compound **4** (3.7 g, 0.0098 mol) was dissolved in a solution of sodium ethoxide (from 0.23 g sodium and 15 ml absolute ethanol) and the solution was heated under reflux for 30 min. The solvent was evaporated in vacuo, some water was added to the residue, and the mixture neutralized (to pH 4) with hydrochloric acid. The separated product was collected and crystallized from dimethylformamide–toluene. Yield: 1.8 g (72%) of the product **5** as white crystals, m.p. 250 °C (dec.). For $C_9H_8N_2OS_3$ (256.4) calculated: 42.16% C, 3.14% H, 10.93% N; found: 42.32% C, 3.34% H, 11.32% N. ^1H NMR spectrum ($(CD_3)_2SO$): 2.90 t, 2 H (H-5); 3.10 t, 2 H (H-6); 3.70 s, 2 H (H-8); 12.30 s, 1 H (NH); 13.30 s, 1 H (NH). ^{13}C NMR spectrum ($(CD_3)_2SO$): 24.00 t (C-5), 24.43 t (C-6), 26.98 t (C-8), 116.54 s (C-4a), 124.47 s (C-4b), 130.47 s (C-8a), 149.38 s (C-9a), 156.83 s (C-4), 172.88 s (C-2).

2-Methylthio-3,5,6,8-tetrahydro-4*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidin-4-one (**6**)

To a suspension of **5** (0.5 g, 0.0019 mol) in acetone (20 ml) was added anhydrous potassium carbonate (0.25 g) followed by methyl iodide (0.38 g, 0.0026 mol). The reaction mixture was stirred at room temperature for 1 h and poured into water. The solid product which precipitated was collected by filtration, dried and recrystallized from dimethylformamide. Yield: 0.42 g (80%) of compound **6** as white crystals, m.p. 285–287 °C. For $C_{10}H_{10}N_2OS_3$ (270.4) calculated: 44.41% C, 3.72% H, 10.36% N; found: 44.19% C, 3.60% H, 10.15% N. ^1H NMR spectrum ($(CD_3)_2SO$): 2.55 s, 3 H (SCH_3); 2.90 t, 2 H (H-5); 3.10 t, 2 H (H-6); 3.90 s, 2 H (H-8); 12.60 s, 1 H (NH).

Ethyl 5,8-Dihydro-2-(methylthio)-4-oxo-4*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]-pyrimidine-3(6*H*)-acetate (**7**)

Method A. A solution of **3** (0.68 g, 0.002 mol) in 1 M aqueous sodium hydroxide (1.5 ml) was treated with methyl iodide (0.57 g, 0.004 mol) and the mixture was stirred at 25 °C. The methylthio

compound **7** started to crystallize almost immediately. After 2 h, it was filtered off, washed with water, dried and crystallized from ethanol. Yield: 0.5 g (71%) of compound **7** as colorless crystals, m.p. 233 °C. For $C_{14}H_{16}N_2O_3S_3$ (356.5) calculated: 47.16% C, 4.52% H, 7.86% N; found: 46.91% C, 4.31% H, 7.68% N. IR spectrum: 1 490, 1 510, 1 680, 1 720, 2 990, 3 000. ^{1}H NMR spectrum ($CDCl_3$): 1.20 t, 3 H ($COOCH_2CH_3$); 2.60 s, 3 H (SCH_3); 2.90 t, 2 H (H-5); 3.30 t, 2 H (H-6); 3.80 s, 2 H (H-8); 4.20 q, 2 H ($COOCH_2CH_3$); 4.90 s, 2 H (NCH_2COO). ^{13}C NMR spectrum ($(CD_3)_2SO$): 13.99 q (SCH_3), 14.85 q ($COOCH_2CH_3$), 24.14 t (C-4), 25.32 t (C-5), 27.59 t (C-7), 60.43 t (NCH_2), 61.52 t ($COOCH_2CH_3$), 111.46 s (C-4a), 122.51 s (C-4b), 129.91 s (C-8a), 145.54 s (C-9a), 164.64 s (C-2), 167.39 s (C-4), 187.73 s (CO ester).

Method B. To a solution of **6** (1 g, 0.0036 mol) in dimethylformamide (10 ml) were added anhydrous potassium carbonate (0.65 g, 0.0047 mol) and ethyl bromoacetate (0.8 g, 0.0047 mol). After stirring at 60 °C for 4 h, the mixture was poured into water, acidified with 2 M hydrochloric acid and extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, and evaporated. The residue was purified using column chromatography (ethanol–toluene 1 : 5). Yield: 0.8 g (61%) of compound **7** as white crystals, m.p. 233 °C. The compound is identical with the compound obtained above.

Ethyl 2-Chloro-5,8-dihydro-4-oxo-4*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidine-3(6*H*)-acetate (**8**)

A suspension of **3** (1 g, 0.0025 mol) in $POCl_3$ (15 ml) was refluxed at 120 °C for 6 h. The reaction mixture became clear. Excess $POCl_3$ was distilled off under reduced pressure. The reaction mixture was cooled and poured into ice/water, the solid product was separated, filtered and passed through a column of silica gel. Elution with toluene–methanol (5 : 1) yielded 0.6 g (68%) of compound **8**, m.p. 147–149 °C. For $C_{13}H_{13}ClN_2O_3S_2$ (344.8) calculated: 45.27% C, 3.79% H, 8.12% N; found: 45.57% C, 3.99% H, 7.87% N. ^{1}H NMR spectrum ($(CD_3)_2SO$): 1.20 t, 3 H ($COOCH_2CH_3$); 2.90 t, 2 H (H-5); 3.20 t, 2 H (H-6); 3.80 s, 2 H (H-8); 4.10 q, 2 H ($COOCH_2CH_3$); 4.90 s, 2 H (CH_2COO).

1-Amino-3,6,7,9-tetrahydro-5*H*-imidazolo[1,2-*a*]thiopyrano[4′,3′:4,5]thieno[2,3-*d*]-pyrimidine-2(1*H*),5-dione (**9**)

Method A. A suspension of **7** (0.4 g, 0.001 mol) in 99% hydrazine hydrate (4 ml) was refluxed gently in absolute ethanol (10 ml). The insoluble solid went into solution within 10 min. After 30 min, when the solid product started to separate, heating was discontinued and the reaction mixture was allowed to cool to room temperature. The solid was filtered, washed with water and ethanol, dried and recrystallized from dimethylformamide. Yield: 0.25 g (76%) of compound **9** as white crystals, m.p. >310 °C. For $C_{11}H_{10}N_4O_2S_2$ (294.3) calculated: 44.88% C, 3.42% H, 19.03% N; found: 44.63% C, 3.21% H, 18.91 N. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.90 t, 2 H (H-6); 3.10 t, 2 H (H-7); 3.80 s, 2 H (NH_2); 5.20 s, 2H (H-3).

Method B. Compound **8** (0.4 g, 0.001 mol) and 99% hydrazine hydrate (2 ml) in ethanol (10 ml) were heated under reflux for 20 min. The reaction mixture was allowed to cool to room temperature. The separated solid product was collected by filtration, washed with ethanol, dried and recrystallized from dimethylformamide. Yield: 0.28 g (76%) of compound **9** as white crystals, m.p. >310 °C.

2-[(Ethoxymethylene)amino]-4,7-dihydro-5*H*-thieno[2,3-*c*]thiopyran-3-carbonitrile (**11**)

A mixture of **10** (ref.[4], 0.5 g, 0.0025 mol) and triethyl orthoformate (20 ml) was refluxed for 4 h. The excess triethyl orthoformate was removed under reduced pressure and the resulting solid product was collected by filtration, dried and recrystallized from methanol. Yield: 0.6 g (94%) of compound **11** as pale yellow crystals, m.p. 89–90 °C. For $C_{11}H_{12}N_2OS_2$ (252.3) calculated: 52.35% C, 4.12% H,

11.10% N; found: 52.18% C, 4.12% H, 10.95% N. IR spectrum: 1 610, 2 200, 2 800, 2 990. ^{1}H NMR spectrum ($CDCl_3$): 1.30 t, 3 H ($OCH_2C\mathbf{H}_3$); 2.90 s, 4 H (H-4, H-5); 3.60 s, 2 H (H-7); 4.40 q, 2 H ($OC\mathbf{H}_2CH_3$); 7.90 s, 1 H (N=CH).

3-Amino-3,5,6,8-tetrahydro-4*H*-thiopyrano[4′,3′:4,5]thieno[2,3-*d*]pyrimidine-4-imine (**12**)

To a solution of **11** (0.8 g, 0.003 mol) in ethanol (20 ml) was added a solution of hydrazine hydrate (4 ml) and the mixture was stirred at room temperature for 45 min. The solid product was collected by filtration, dried and recrystallized from ethanol. Yield: 0.52 g (69%) of compound **12** as colorless crystals, m.p. 178–180 °C. For $C_9H_{10}N_4S_2$ (238.3) calculated: 45.35% C, 4.22% H, 23.51% N; found: 45.59% C, 3.99% H, 23.30% N. IR spectrum: 1 410, 1 460, 1 600, 2 990, 3 000, 3 150, 3 250, 3 400. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.90 t, 2 H (H-5); 3.20 t, 2 H (H-6); 3.90 s, 2 H (H-8); 5.60 s, 2 H (NH_2); 7.10 s, 1 H (NH); 7.90 s, 1 H (H-2). ^{13}C NMR spectrum ($(CD_3)_2SO$): 24.87 t (C-5), 25.02 t (C-6), 28.36 s (C-8), 120.51 s (C-4a), 127.75 s (C-4b), 130.87 s (C-8a), 148.35 s (C-9a), 151.41 s (C-2), 154.68 s (C-4).

10,11-Dihydro-8*H*-thiopyrano[4′,3′:4,5]thieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine (**13a**)

Compound **12** (0.3 g, 0.0012 mol) was refluxed with triethyl orthoformate (10 ml) for 4 h. The excess triethyl orthoformate was removed under reduced pressure and the resulting solid product was collected by filtration, dried and recrystallized from ethanol. Yield: 0.23 g (74%) of compound **13a** as yellow crystals, m.p. 191–193 °C. For $C_{10}H_8N_4S_2$ (248.3) calculated: 48.36% C, 3.24% H, 22.56% N; found: 48.10% C, 3.25% H, 22.40% N. IR spectrum: 1 540, 1 620, 2 990, 3 050. ^{1}H NMR spectrum ($CDCl_3$): 3.10 t, 2 H (H-11); 3.60 t, 2 H (H-10); 3.90 s, 2 H (H-8); 8.30 s, 1 H (H-2); 9.20 s, 1 H (H-5).

2-Methyl-10,11-dihydro-8*H*-thiopyrano[4′,3′:4,5]thieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine (**13b**)

Compound **12** (0.3 g, 0.001 mol) and triethyl orthoacetate (8 ml) were treated as described for the preparation of compound **13a**. The yield of the recrystallized compound **13b** was 68%, m.p. 228–230 °C. For $C_{11}H_{10}N_4S_2$ (262.3) calculated: 50.35% C, 3.84% H, 21.35% N; found: 49.99% C, 3.60% H, 21.18% N. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.55 s, 3 H (CH_3); 3.00 t, 2 H (H-11); 3.30 t, 2 H (H-10); 4.10 s, 2 H (H-8); 9.50 s, 1 H (H-5).

2-Trichloromethyl-10,11-dihydro-8*H*-thiopyrano[4′,3′:4,5]thieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]-pyrimidine (**14**)

A mixture of **12** (0.3 g, 0.0012 mol) and trichloroacetonitrile (5 ml) was heated under reflux for 20 h. After cooling, the solid product was collected by filtration, washed with a small amount of ethanol and recrystallized from ethanol. Yield: 0.3 g (65%) of compound **14** as colorless crystals, m.p. 250–252 °C (dec.). For $C_{11}H_7Cl_3N_4S_2$ (365.7) calculated: 36.12% C, 1.92% H, 15.32% N; found: 36.32% C, 1.99% H, 15.51% N. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.90 t, 2 H (H-11); 3.20 t, 2 H (H-10); 4.00 s, 2 H (H-8); 8.70 s, 1 H (H-5).

2-Chloromethyl-10,11-dihydro-8*H*-thiopyrano[4′,3′:4,5]thieno[3,2-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine (**15**)

Chloroacetyl chloride (0.3 g, 0.0026 mol) was added dropwise under stirring to a solution of **12** (0.3 g, 0.0012 mol) in dimethylformamide (6 ml). Then the reaction mixture was heated on a steam bath for 2 h and – after cooling – poured into ice/water (50 ml). The solid product was collected by filtration, washed with water and recrystallized from ethanol. Yield: 0.3 g (81%) of compound **15** as colorless

crystals, m.p. 206–208 °C. For $C_{11}H_9ClN_4S_2$ (296.8) calculated: 44.51% C, 3.05% H, 18.87% N; found: 44.31% C, 2.89% H, 18.69% N. ^{1}H NMR spectrum ($(CD_3)_2SO$): 3.00 t, 2 H (H-11); 3.30 t, 2 H (H-10); 4.10 s, 2 H (H-8); 5.00 s, 2 H (CH_2Cl); 9.60 s, 1 H (H-5).

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crystals, m.p. 206–208 °C. For $C_{11}H_9ClN_4S_2$ (296.8) calculated: 44.51% C, 3.05% H, 18.87% N; found: 44.31% C, 2.89% H, 18.69% N. ^{1}H NMR spectrum ($(CD_3)_2SO$): 3.00 t, 2 H (H-11); 3.30 t, 2 H (H-10); 4.10 s, 2 H (H-8); 5.00 s, 2 H (CH_2Cl); 9.60 s, 1 H (H-5).

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