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ВЗАИМОДЕЙСТВИЕ 3-АРОИЛ-1*H*-ПИРРОЛО[2,1-*c*][1,4]БЕНЗОКСАЗИН-1,2,4-ТРИОНОВ С ТИОФЕНАМИ ГЕВАЛЬДА

Исследованы реакции 3-ароил-1Н-пирроло[2,1-с][1,4]бензоксазин-1,2,4-трионов с рядом тиофенов Гевальда. Установлено, что в результате этих реакций образуются замещенные (Z)-этил 2(2,4-диоксо-3-(2-оксо-2Н-бензо[b][1,4]оксазин-3(4Н)-илиден)-4-арилбутанамидо)-тиофен-3-карбоксилаты.

Ключевые слова: гетарено[e]пиррол-2,3-дионы; тиофены Гевальда; рециклизация

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REACTIONS OF 3-AROYL-1*H*-PYRROLO[2,1-*c*][1,4]BENZOXASINE-1,2,4-TRIONES WITH GEWALD THIOPHENES

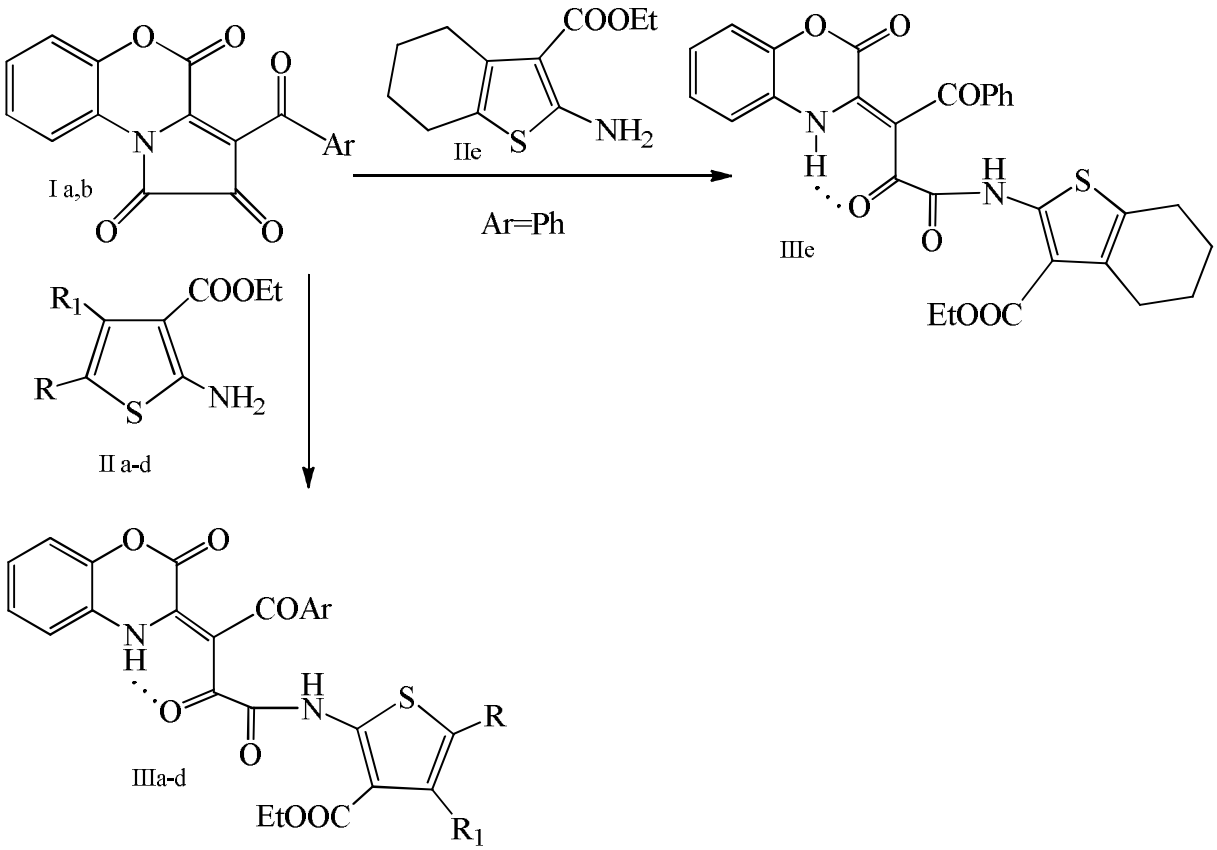
The reactions of 3-aroyl-1H-pyrrolo[2,1-c][1,4]benzoxazine-1,2,4-triones with a number of Gewald thiophenes were studied. It was established that as a result of these reactions, substituted (Z)-ethyl 2(2,4-dioxo-3-(2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)-4-arylbutanamido)thiophene-3-carboxylates.

Keywords: hetareno[e]pyrrole-2,3-diones; Gewald's thiophenes; recyclization

Gewald's thiophenes [1] are widely used as convenient "building blocks" for the synthesis of condensed heterocycles.

It was previously discovered that reactions of these reagents with pyrroloquinoxalinetriones lead to pharmacologically active products [2], while the interaction of 3-aroyl-1H-pyrrolo [2,1-c][1,4]benzoxazine-1,2,4-triones with Gewald's thiophenes have not been previously studied.

It was found that in the reaction of 3-aroyl-1H-pyrrolo[2,1-c][1,4]benzoxazine-1,2,4-triones with a number of Gevald thiophenes, carried out by short boiling in anhydrous acetonitrile, gives the products of the initial nucleophilic addition of the reagent to the carbon atom at position 1 of the pyrrolbenzoxazintrione molecule, followed by the disclosure of the pyrroldione ring via the C^1-N^{10} bond and the formation of recycling products - substituted (Z)-ethyl 2(2,4-dioxo-3-(2-oxo-2H-benzo[b][1,4] oxazin-3(4H)-ylidene)-4-arylbutan-amido)thiophene-3-carboxylates (IIIa-e)



Ar=Ph (Ia), 4-MeC_6H_4 (Ib); R=R_1=Me, Ar=4-MeC_6H_4 (IIa, IIIa), R=Ph, R_1=Me, Ar=4-MeC_6H_4 (IIb, IIIb), R=Me, R_1=Ph, Ar=4-MeC_6H_4 (IIc, IIIc), R= R_1=Ph, Ar=4-MeC_6H_4 (IId, IIId)

Compounds III (a-e) are crystalline substances of orange color, insoluble in common organic solvents, insoluble in water and alkanes. They do not give a positive enols test (cherry color) with an alcoholic solution of iron (III) chloride.

The structure of the synthesized compounds was confirmed by the IR and NMR spectroscopy data.

The IR spectra of compounds III (a-e) contains bands of stretching vibrations of NH groups around 3209-3280 cm^{-1}, carbonyl ester groups around 1774-1778 cm^{-1}, carbonyl groups of the CONH side chain, C^2=O, and aroyl fragments in the area of 1572-1656 cm^{-1}, the band "amide II" around 1511-1530 cm^{-1}.

In the ^{1}H NMR spectra of compounds III (a-e), in addition to the signals of aromatic protons and related groups, there are singlets of the proton of the amide NH group of the side chain in the region of 12.24-12.39 ppm, an extended singlet of the proton of the N^{1}H group in the region of 14.04-14.12 ppm.

Experimantal data

IR spectra of the synthesized compounds were recorded on an FSM-1201 spectrophotometer in liquid paraffin. ^{1}H NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer in DMSO-d_6; HMDS was used as the internal standard. The identity of the synthesized compounds was confirmed by thin layer chromatography on Silufol plates, eluents — ethyl acetate, ethyl acetate-benzene, 1:5, chromatograms showed iodine vapor.

(Z)-Ethyl 2-(2,4-dioxo-3-(2-oxo-2H-benzo[b][1,4]oxasine-3(4H)-ylidene)-4-(4-tolylbutanamido)-4,5-dimethylthiophene-3-carboxylate (IIIa)

To a solution of 0.005 mol of 3-(4-methylbenzoyl)-1*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione [3], in anhydrous acetonitrile were added 0.005 mol of ethyl-2-amino-4,5-dimethylthiophene-3-carboxylate [1], heated for 5-10 minutes, after which the reaction mixture was left for a day, the precipitate of compound (IIIa) was filtered off, recrystallized from anhydrous acetonitrile. Yield 84%, m.p. = 253-255 ° C. IR spectrum (FSM-120, liquid paraffin, ν, cm^{-1}): 3209, 3236 (NHCO, NH), 1775 (COO), 1689 (CONH), 1668 (COAr), 1579 wide C^2 = O), 1521 (amide II). ^{1}H NMR spectrum, δ, ppm: 1.37 t (3H, CH_3), 1.39 t (3H, CH_3), 2.36 s (6H, 2CH_3), 4.38 q (2H, CH_2), 7.15-7.70 gr.s. (8H, 2C_6H_4), 12.30 s (1H, NHCO), 14.10 br.s. (1H, NH). Found, %: C 63.18; H 4.52; N 5.25. $C_{28}H_{24}N_2O_7S$. Calculated, %: C 63.15; H 4.54; N 5.26.

(Z)-Ethyl 2-(2,4-dioxo-3-(2-oxo-2H-benzo[b][1,4]oxasine-3(4H)-ylidene)-4-(4-tolylbutanamido)-4-methyl-5-phenylthiophene-3-carboxylate (IIIb)

Synthesized similarly. Yield – 79%, T.пл. = 202-203°C.

IR spectrum (FSM-120, liquid paraffin, ν, cm^{-1}): 3190, 3274 (NHCO, NH), 1775 (COO), 1680 (CONH), 1667 (COAr), 1572 ш (C^2 = O), 1511 (amide II). ^{1}H NMR spectrum, δ, ppm: 1.34 t (3H, CH_3), 1.42 t (3H, CH_3), 2.34 s (6H, 2CH_3), 4.34 q (2H, CH_2), 7.30-7.96 gr.s. (8H, 2C_6H_4), 12.32 s (1H, NHCO), 14.10 br.s. (1H, NH). Found, %: C 66.65; H 4.41; N 4.72. $C_{33}H_{26}N_2O_7S$. Calculated, %: C 66.66; H 4.41; N 4.71.

(Z)-Ethyl 2-(2,4-dioxo-3-(2-oxo-2H-benzo[b][1,4]oxasine-3(4H)-ylidene)-4-(4-tolylbutanamido)-5-methyl-4-phenylthiophene-3-carboxylate (IIIc)

Synthesized similarly. Yield – 81%, m.p. = 230-232°C. IR spectrum (FSM-120, liquid paraffin, ν, cm^{-1}): 3175, 3230 (NHCO, NH), 1774 (COO), 1690 (CONH), 1658 (COAr), 1586 ш (C^2 = O), 1521 (amide II). ^{1}H NMR spectrum, δ, ppm: 0.73 t (3H, CH_3), 2.01 t (3H, CH_3), 2.33 s (6H, 2CH_3), 3.94 q (2H, CH_2), 7.10-7.76 gr.s. (8H, 2C_6H_4), 12.24 s (1H, NHCO), 14.04 br.s. (1H, NH). Found, %: C 66.65; H 4.43; N 4.71. $C_{33}H_{26}N_2O_7S$. Calculated, %: C 66.66; H 4.41; N 4.71.

(Z)-Ethyl 2-(2,4-dioxo-3-(2-oxo-2H-benzo[b][1,4]oxasine-3(4H)-ylidene)-4-(4-tolylbutanamido)-4,5-diphenylthiophene-3-carboxylate (IIId)

Synthesized similarly. Yield – 78%, m.p. = 263-265°C. IR spectrum (FSM-120, liquid paraffin, ν, cm^{-1}): 3212, 3280 (NHCO, NH), 1777 (COO), 1685 (CONH), 1656 (COAr), 1580 ш (C^2 = O), 1520 (amide II). ^{1}H NMR spectrum, δ, ppm: 0.77 t (3H, CH_3), 1.29 t (3H, CH_3), 2.35 s (6H, $2CH_3$), 3.98 q (2H, CH_2), 7.04-7.84 gr.s. (8H, $2C_6H_4$), 12.39 s (1H, NHCO), 14.12 br.s. (1H, NH). Found, %: C 69.53; H 4.29; N 4.27. $C_{38}H_{28}N_2O_7S$. Calculated, %: C 69.50; H 4.30; N 4.27.

(Z)-Ethyl 2-(2,4-dioxo-3-(2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxasine-3-yl)-4-(phenylbutanamido)-4,5,6,7-tetrahydrobenzo [b]thiophene-3-carboxylate (IIIe)

Synthesized similarly. Yield – 71%, m.p. = 230-232°C.

IR spectra (FSM-120, liquid paraffin, *v*, cm^{-1}): 3210, 3230 (NHCO, NH), 1778 (COO), 1690 (CONH), 1665 (CO_{Ar}), 1579 ш (C_2=O), 1530 (amide II). ^{1}H NMR spectrum, δ, ppm.: 1.70 gr.s. (4H, $2CH_2$), 2.79 s (2H, CH_2), 4.04 q (2H, CH_2), 7.14-7.79 gr.s. (8H, $2C_6H_4$), 12.33 s (1H, NHCO), 14.10 s (1H, NH). Found, %: C 63.97; H 4.45; N 5.12. $C_{29}H_{24}N_2O_7S$. Calculated, %: C 63.96; H 4.44; N 5.14.

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