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Reactions of Pyrrole-1- and Pyrrole-2-carbodithioates with Activated Acetylenes

L. N. Sobenina, A. P. Demenev, A. I. Mikhaleva, V. N. Elokhina, Z. V. Stepanova, A. G. Mal'kina, I. A. Ushakov, and B. A. Trofimov

Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033 Russia

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Abstract—Pyrrole-1- and pyrrole-2-carbodithioates react with activated alkenes (KOH–DMSO, room temperature) along the nucleophilic addition mechanism regio- and stereospecifically to afford pyrrole-1- and pyrrole-2-carbodithioethenes. The adducts of pyrrole-2-carbodithioates under the reaction conditions undergo intramolecular cyclization into pyrrolothiazoles derivatives.

Unlike the known in detail addition reactions across multiple bonds of alkanecarbodithioates [1] similar reactions of their pyrrole analogs, pyrrole-1- and pyrrole-2-carbodithioates are less investigated [2, 3]. We showed formerly that pyrrole-2-carbodithioates generated in situ from pyrroles and carbon disulfide in the system KOH–DMSO readily added to the acrylic acid derivatives affording functionally substituted pyrrole-2-carbodithiopropionates in 40–60% yield [3]. In contrast to pyrrole-2-carbodithioates their isomers, pyrrole-1-carbodithioates (essentially, dithiocarbamates), under similar conditions in anion form did not to the acrylic acid derivatives. However the pyrrole-1-dithiocarboxylic acid proper obtained from the corresponding salt reacted with acrylamide in aqueous DMSO to furnish 2-carbamoylethylpyrrole-1-carbodithioate in 95% yield [3].

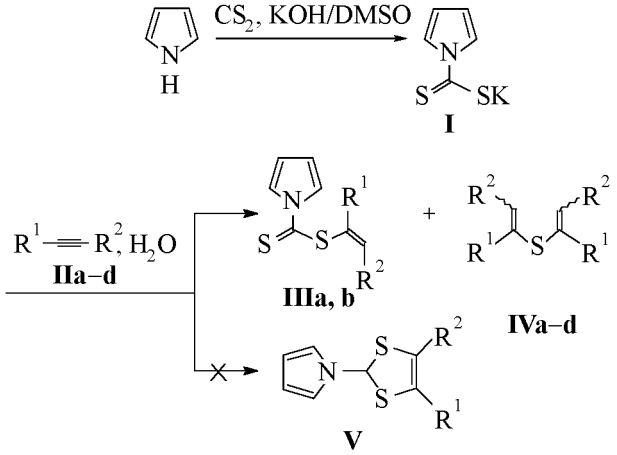
The study of the laws of pyrrolecarbodithioate anions addition to acetylenes and of the influence of various factors on the reaction result can provide important information both for forecasting the reactivity of these valuable building blocks and for development of preparation procedures for biologically active compounds including sulfur-containing heterocycles.

The reactions of dithioate anions with activated acetylenes may proceed as anionic 1,3-cycloaddition and as nucleophilic addition [1]. When the central atom in the system $S=C-S^-$ contains aromatic or heteroaromatic substituents that stabilize anion, the typical reaction path is 1,3-anionic cycloaddition [2, 4]. For instance, salts of pyrrole-1, thiophene-2-, furan-2-, and naphthalene-1-dithiocarboxylic acids react with dimethyl acetylenedicarboxylate selectively to afford cycloadducts [2].

The target of this work was the study of the direction of the reaction between pyrrole-1- and pyrrole-2-carbodithioates and electrophilic acetylenes depending on the reaction conditions, substituents in the dithioate moiety and alkynes.

The study was carried out with the salts of N- and C-pyrrolecarbodithioates generated respectively from pyrrole and 4,5,6,7-tetrahydroindole in the system KOH–DMSO–CS_2. Assuming that in reactions of 1,3-anionic cycloaddition an important role plays the nucleophilic attack we used as dipolarophiles acetylenes activated with acceptor substituents: ethyl propiolate (**IIa**), benzoylacetylene (**IIb**), phenylcyanoacetylene (**IIc**), phenylbenzoylacetylene (**IId**), and phenyl(2-furoyl)acetylene (**IIe**).

We established that the reaction of pyrrole-1-carbodithioate (**I**) with ethyl propiolate (**IIa**) and benzoylacetylene (**IIb**) in DMSO (room temperature, 2 h)



R^1 = H, R^2 = CO_2Et (**a**), COPh (**b**); R^1 = Ph, R^2 = CN (**c**), COPh (**d**).

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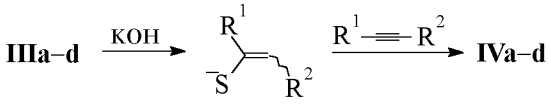
resulted in normal adducts, pyrrole-1-carbodithioethenes (**IIIa, b**) in 10% (**IIIa**) and 18% (**IIIb**) yields. The main reaction products are substituted divinyl sulfides **IVa, b** (a mixture of *Z,Z*-, *Z,E*- and *E,E*-isomers).

The latter apparently are secondary products arising from solvolysis of adducts **IIIa, b** with alkali formed in the reaction [5] followed by nucleophilic addition of the vinylsulfide anions to the second acetylene molecule.



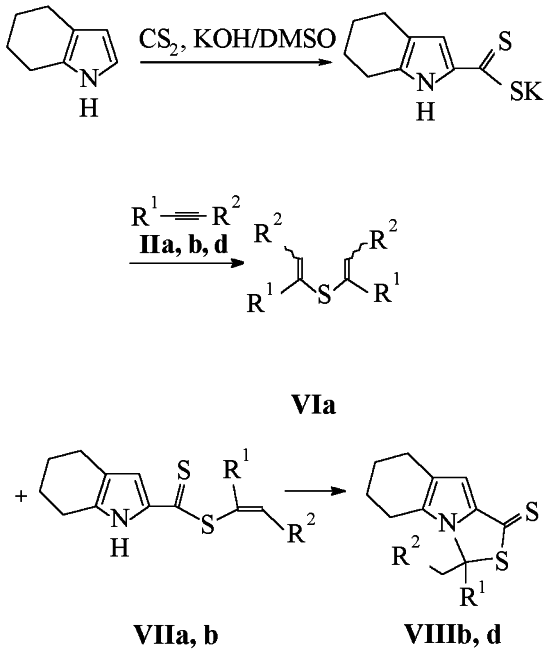
To prevent the cleavage of the C–S bond providing divinyl sulfides **IVa, b** and to increase the yield of adducts **IIIa, b** we tried to carry out the reaction under conditions ensuring fast extraction of the primary products into organic phase (two-phase system aqueous dimethyl sulfoxide–ethyl ether). However in this case divinyl sulfides **IVa, b** still were the main products. Basic cleavage of the primary adducts **IIIa, b** was successfully prevented by addition to the reaction mixture diluted with water 3-fold molar excess of acetic acid (with respect to dithioate **I**). Under such conditions the yield of pyrrole-1-carbodithioethenes **IIIa, b** was respectively 62 and 65%.

The acetylenes activated from both sides with electronegative (π^- or δ^-) substituents are known to react with the anions of dithiocarboxylic acids to yield mainly the products of 1,3-anionic cycloaddition of type **V**. However under conditions studied we failed to obtain cycloadducts of anion **I** with disubstituted acetylenes **IIc, d**. The only reaction products here were the corresponding divinyl sulfides **IVc, d**, also in the presence of the acetic acid. Note also that in reaction at standard conditions acetylene **IIg** did not react completely.

Obviously due to reduced reactivity of the disubstituted acetylenes (steric hindrances) the competing solvolysis of anions **I** results in sulfide ions that reacting with acetylenes afford divinyl sulfides **IVc, d**.

The configuration of adducts was estimated from ^{1}H NMR spectra: Compounds **IIIa, b** were *Z*-isomers. Therefore the studied reaction of pyrrole-1-carbodithioate with terminal acetylenes proceeds as a normal concerted nucleophilic trans-addition.

In contrast to pyrrole-1-carbodithioate (**I**) 4,5,6,7-tetrahydroindol-2-carbodithioate (**VI**) adds to terminal **IIb** and internal **IIe** acylacetylenes affording in 46–47% yield functionally substituted pyrrolothiazoles VIIIb, e, products of intramolecular cyclization of the intermediately formed 2-acylethenylpyrrole-2-carbodithioates **VIIb, e** that are detected only as traces. The reaction is easily performed in a two-phase system (aqueous dimethyl sulfoxide–ethyl ether) in the presence of KOH at 25°C.



R^1 = **H, R**^{2} = **CO$_2$Et (a)**, COPh (**b**); R^1 = Ph, R^2 = 2-furoyl (**e**).

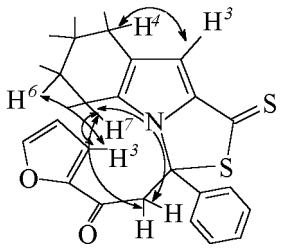
However with ethyl propiolate **IIa** pyrrole-2-carbodithioate **VI** under the given conditions reacts selectively to form sulfide **IVa**. Ethyl-(4,5,6,7-tetrahydro-2-indolylthiocarbonylthio)-2-propenoate (**VIIa**) we succeeded to obtain only after neutralization of the reaction mixture with acetic acid.

Thus our investigations demonstrated that the salts of pyrrole-1- and pyrrole-2-dithiocarboxylic acids react with activated alkynes solely along nucleophilic addition mechanism strictly regio- and stereospecifically notwithstanding the position of the dithioate function in the pyrrole ring.

The structure of all compounds synthesized was proved by ^{1}H, ^{13}C NMR, and IR spectra, the composition was confirmed by elemental analysis. For instance, in the IR spectra of compounds **IIIb, IVb, VIIb** the strong absorption band of the carbonyl group appears in the region 1638–1647 cm^{-1}. The shift of this band to longwave region is due to an additional conjugation of the carbonyl group with the

double bond. In compounds **VIIIb, e** where this bond is saturated this band shifts into 1671 cm^{-1} region, common for carbonyl groups conjugated only with benzene or furan ring.

The signals from vinyl protons in compounds **IIIa, b** and **VIIa, b** appear as two doublets in the region 8.38–8.94 (COCH=) and 6.24–7.45 (SCH=) ppm respectively with a coupling constant 10.3 Hz confirming the Z-configuration of the compounds. The pyrrole proton H^3 in compound VIIa is in a form of a doublet at 7.06 ppm, *J* 2.6 Hz, and in thiazoles **VIIIb, e** gives a singlet at 6.75 ppm. In order to assign the pyrrole protons signals and to establish the structure of compounds **VIIIb, e** for compound **VIIIe** was registered two-dimensional ^1H NMR spectrum in NOESY mode. Thus in one possible conformation of this compound the proton H^3 of the pyrrole ring should have a cross-peak with the proton H^4 of the cyclohexane ring.



VIIIe

The protons of CH_2 group have cross-peaks with H^7 proton of the cyclohexane ring, o-proton of benzene ring, and H^3 of furan ring. The H^3 proton of the furan ring has cross-peaks with H^6 and H^7 of the cyclohexane ring.

The vinyl protons signals in sulfides **IVa, b** spectra appear as two doublets in the region 7.08–7.95 (H_α) and 5.94–7.42 (H_β) ppm respectively. In the ^1H NMR spectra of sulfides **IVc** and **IVd** are observed individual signals from olefin protons (5.59 and 7.13 ppm respectively) evidencing the presence of a single isomer, presumably of Z-configuration if the reaction occurs as a normal concerted trans-addition. The *Z,Z*-configuration of sulfide **IVc** is also proved by coincidence of its melting point with the published one [6].The structure of compound **IVd** was confirmed by NMR spectroscopy on ^1H and ^{13}C nuclei with the use of two-dimensional procedures TOCSY, HSQC, and HMBC [7, 8]. For instance, in its HSQC spectrum the projections corresponding to the axis F_1 (along ^1H channel) provided a possibility of an unambiguous assignment of the protons signals to the presumed structure. For the assignment of carbon signals in the aromatic systems of this compound was used heteronuclear two-dimensional NMR spectroscopy HSQC [7], and for the quaternary carbon atoms the HMBC procedure [8].

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on spectrometer JFS-25 in the region 400–4000 cm^{-1} from KBr pellets. ^1H and ^{13}C NMR spectra were registered on Jeol FX-90Q (90 MHz) and Bruker DPX 250 (250.13 MHz for ^1H and 62.9 MHz for ^{13}C), solvent chloroform, internal reference HMDS. In recording two-dimensional spectra NOESY was used a standard procedure with mixing period 1.2 s [9]. The analysis of the reaction mixtures and testing for purity of compounds obtained was performed by TLC on Silufol UV-254 plates, eluent hexane–ethyl ether, 1:1. Preparative separation of compounds was carried out by column chromatography om alumina, eluent hexane–ethyl ether.

Pyrrole used was a commercial product, 4,5,6,7-tetrahydroindole was prepared by Trofimov reaction [10].

Ethyl 3-(1-pyrrolylthiocarbonylthio)propenoate (IIIa) and diethyl 3,3'-thiobisacrylate (IVa). (a) A mixture of 0.67 g (10 mmol) of pyrrole and 0.56 g (10 mmol) of KOH in 10 ml of DMSO was stirred for 0.5 h, then was added 1.52 g (20 mmol) of carbon disulfide. The reaction mixture was left standing at room temperature for 2 h, and then was added 0.98 g of acetylene IIa, and the mixture was stirred for 2 h. The reaction mixture was afterwards diluted with water (50 ml), and the reaction products were extracted into ether. On removing the solvent the residue was subjected to column chromatography (eluent hexane) to isolate 0.24 g (10%) of pyrrole **IIIa**, mp 44–45°C. IR spectrum, ν, cm^{-1}: 527, 562, 590, 604, 673, 697, 714, 741, 798, 810, 949, 962, 1017, 1026, 1045, 1097, 1112, 1118, 1166, 1215, 1257, 1284, 1327, 1348, 1404, 1444, 1471, 1487, 1554, 1586, 1702, 2851, 2920, 2981, 3012, 3063, 3142. ^1H NMR spectrum ($CDCl_3$, δ, ppm): 1.31 t (3H, CH_3), 4.24 q (2H, CH_2), 6.24 d.d (1H, SCH=, *J* 10.3 Hz), 6.36 t (2H, H^3, H^4), 7.76 t (2H, H^2, H^5), 8.38 d.d (1H, CH=, *J* 10.3 Hz). Found, %: C 49.37; H 4.99; N 5.41; S 25.85. $C_{10}H_{11}NO_2S_2$. Calculated, %: C 49.77; H 4.59; N 5.80; S 26.57. Then from the column (eluent ether) was isolated 0.6 g (52%) of orange crystals of the isomers mixture of diethyl 3,3'-thiobisacrylate (**IVa**), mp 49–50°C. After wash-

ing the crystals with methanol remain colorless crystals of the *Z,Z*-isomer of sulfide **IVa**, mp 104–105°C.

IR spectrum, ν, cm^{-1}: 673, 694, 712, 787, 801, 816, 829, 967, 1030, 1045, 1115, 1166, 1190 1222, 1246, 1351, 1372, 1406, 1451, 1458, 1480, 1564, 1597, 1684, 1698, 2903, 2934, 2980, 3034, 3069. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.31 t (6H, CH_3), 4.22 q (4H, CH_2), 5.95 d.d (2H, SCH=, *J* 10.3 Hz), 7.08 d.d (2H, =$CHCO_2$Et, *J* 10.3 Hz). Found, %: C 52.43; H 5.89; S 14.75. $C_{10}H_{14}O_4S$. Calculated, %: C 52.17; H 6.12; S 13.91.

(b) A mixture of 0.67 g (10 mmol) of pyrrole and 0.56 g (10 mmol) of KOH in 10 ml of DMSO was stirred for 0.5 h, then was added 1.52 g (20 mmol) of carbon disulfide. The reaction mixture was left standing at room temperature for 2 h, and then was added 10 ml of H_2O and 0.98 g of acetylene **IIa**, and the mixture was stirred for 2 h at room temperature. The reaction mixture was afterwards diluted with water (50 ml), and the reaction products were extracted into ether. On removing the solvent the residue was subjected to column chromatography (eluent hexane) to isolate 0.87 g (30%) of pyrrole **IIIa**, and then (eluent ether) 0.31 g (27%) of orange crystals of sulfide **IVa**, mp 51–52°C.

(c) The reaction was carried out as in procedure b, but to the dimethyl sulfoxide–water solution was added 2 ml of acetic acid. As a result the yield of pyrrole **IIIa** was 1.5 g (62%).

2-Benzoylvinyl-1-pyrrolecarbodithioate (IIIb) and 3,3′-thiobis(1-phenyl-2-propenone) (IVb). From 0.067 g (1 mmol) of pyrrole **I** and 0.13 g (1 mmol) of acetylene **IIb** along procedure a described for compound **IIIa** we obtained first 0.05 g (18%) of pyrrole **IIIb**, mp 88–89°C. IR spectrum, ν, cm^{-1}: 528, 603, 675, 687, 720, 732, 747, 804, 884, 951, 1012, 1024, 1052, 1095, 1114, 1121, 1194, 1241, 1287, 1329, 1368, 1404, 1444, 1469, 1553, 1579, 1597, 1647, 2851, 2920, 3063, 3151. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 6.38 t (2H, H^3, H^4), 7.45 d.d (1H, SCH=, *J* 10.3 Hz), 7.53 m (3H, H arom), 7.84 t (2H, H^2, H^5), 8.00 m (2H, H arom), 8.65 d.d (1H, -OCCH=, *J* 10.3 Hz). Found, %: C 61.03; H 4.33; N 4.70; S 22.79. $C_{14}H_{11}NOS_2$. Calculated, %: C 61.51; H 4.06; N 5.12; S 23.46. Then was separated 0.08 g (54%) of orange crystals of the *E,Z*-isomers mixture of 3,3′-thiobis(1-phenyl-2-propenone) (**IVb**). mp 149°C. IR spectrum, ν, cm^{-1}: 650, 669, 695, 733, 769, 778, 812, 872, 883, 929, 959, 1016, 1034, 1179, 1211, 1240, 1263, 1446, 1524, 1564, 1577, 1596, 1638, 2922, 3054. ^{1}H NMR spectrum (CD_3OD, δ, ppm): 7.42 d.d (1H, SCH=, *J* 9.7 Hz), 7.46 d.d (1H, SCH=, *J* 15.3 Hz), 7.52–7.58 m (6H, H arom), 7.95 d.d (1H, COCH=, *J* 9.75 Hz), 8.00 m (4H, H arom), 8.15 d (1H, COCH=, *J* 15.3 Hz). Found, %: C 72.96; H 4.68; S 11.25. $C_{18}H_{14}O_2S$. Calculated, %: C 73.47; H 4.76; S 10.88.

Along procedure b described under compound **IIIa** from 0.067 g (1 mmol) of pyrrole and 0.13 g (1 mmol) of acetylene **IIb** we obtained 0.1 g (38%) of pyrrole **IIIb** and 0.05 g (34%) of sulfide **IVb**.

Along procedure *c* described under compound **IIIa** from 0.067 g (1 mmol) of pyrrole and 0.13 g (1 mmol) of acetylene **IIb** we obtained 0.17 g (65%) of pyrrole **IIIb**. 3,3′-Thiobiscinnamonitrile (**IVc**).

Along procedure c described under compound **IIIa** from 0.34 g (5 mmol) of pyrrole, 0.28 g (5 mmol) of KOH, 0.76 g (10 mmol) of carbon disulfide, 0.64 g (5 mmol) of acetylene **IIc**, and 1 ml of acetic acid we obtained 0.46 g (64%) of sulfide **IVc**, mp 177–178°C (publ.: 176–178°C [6]). IR spectrum, ν, cm^{-1}: 693, 754, 765, 819, 1020, 1053, 1117, 1229, 1321, 1402, 1445, 1462, 1487, 1559, 1634, 2214, 2920, 3042. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 5.59 s (2H, CH), 7.09, 7.19, 7.26 m (10H, H arom). Found, %: C 74.57; H 4.19; N 9.54; S 11.17. $C_{18}H_{12}N_2S$. Calculated, %: C 74.97; H 4.17; N 9.72; S 11.11.

3,3′-Thiobis(1,3-diphenyl-2-propenone) (IVd). Along procedure c described under compound **IIIa** from 0.34 g (5 mmol) of pyrrole, 0.28 g (5 mmol) of KOH, 0.76 g (10 mmol) of carbon disulfide, and 1.03 g (5 mmol) of acetylene **IId** we obtained 0.54 g (48%) of sulfide IVd, mp 176–177°C. IR spectrum, ν, cm^{-1}: 473, 562, 575, 619, 652, 665, 690, 752, 766, 846, 914, 941, 999, 1020, 1038, 1179, 1208, 1234, 1303, 1332, 1445, 1485, 1530, 1558, 1576, 1595, 1642. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 7.00 m (4H, H arom), 7.08 m (4H, H arom), 7.13 s (2H, CH), 7.20 m (2H, H arom), 7.50 m (4H, H arom of benzoyl), 7.55 m (2H, H arom of benzoyl), 8.03 m (4H, H arom of benzoyl). ^{13}C NMR spectrum ($CDCl_3$, δ_C, ppm): 124.8 (C^2), 128.1 ($C^{2,6}$, Ph), 128.1 ($C^{3,5}$, Ph), 128.5 ($C^{2,6}$, PhCO), 128.7 ($C^{3,5}$, PhCO), 128.9 (C^4, Ph), 132.7 (C^4, PhCO), 138.3 (C_{ipso}, PhCO), 140.8 (C_{ipso}, Ph), 155.7 (C^1), 188.8 (C=O). Found, %: C 81.36; H 4.52; S 7.65. $C_{30}H_{22}O_2S$. Calculated, %: C 80.71; H 4.93; S 7.17. By column chromatography (eluent hexane) was recovered 0.25 g of acetylene **IId** (conversion 76%).

Ethyl 3-(4,5,6,7-tetrahydro-1H-indol-2-yl-thiocarbonylthio-2-propenoate) VIIa. Along procedure

a described under compound **IIIa** from 1.2 g (10 mmol) of 4,5,6,7-tetrahydroindole, 0.56 g (10 mmol) of KOH, 1.52 g (20 mmol) of carbon disulfide, and 0.98 g (10 mmol) of acetylene **IIa** we obtained 0.48 g (42%) of orange crystals of a mixture of *Z,Z*-, *E,E*-, and *Z,E*-isomers of sulfide **IVa**.

Along procedure *c* described under compound **IIIa** from 1.2 g (10 mmol) of 4,5,6,7-tetrahydroindole, 0.56 g (10 mmol) of KOH, 1.52 g (20 mmol) of carbon disulfide, 0.98 g (10 mmol) of acetylene **IIa**, and 1 ml of acetic acid we obtained 0.1 g (9%) of sulfide **IVa** and 1.5 g (51%) of pyrrole **VIIa**, mp 118°C.

IR spectrum, ν, cm^{-1}: 561, 685, 717, 797, 809, 830, 850, 925, 959, 982, 1038, 1148, 1169, 1187, 1216, 1261, 1307, 1330, 1344, 1364, 1425, 1448, 1463, 1520, 1553, 1583, 1694, 1703, 2849, 2922, 3059, 3729, 3314. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.31 t (3H, CH_3), 1.77 m (4H, $C^{5,6}H_2$), 2.55 m (4H, $C^{4,7}H_2$), 4.24 q (2H, CH_2), 6.24 d.d (1H,SCH=, *J* 10.8 Hz), 7.06 d (1H, H^3), 8.63 d.d (1H, CH= , *J* 10.8 Hz), 9.40 br.s (1H, NH). Found, %: C 56.44; H 6.12; N 4.56; S 20.95. $C_{14}H_{17}NO_2S_2$. Calculated, %: C 56.92; H 5.80; N 4.74; S 21.71.

2-Benzoylvinyl 4,5,6,7-tetrahydroindol-2-carbodithioate (VIIb) and 2-(1-thioxo-5,6,7,8-tetrahydro-1H-[1,3]thiazolo[3,4-a]indol-3-yl)-1-phenylethanone (VIIIb). Along procedure c described under compound **IIIa** from 0.12 g (1 mmol) of 4,5,6,7-tetrahydroindole, 0.06 g (1 mmol) of KOH, 0.15 g (2 mmol) of carbon disulfide, and 0.13 g (1 mmol) of acetylene **IIb** was obtained 0.01 g of oily substance containing pyrrole **VIIb**, and 0.15 g (47%) of pyrrole **VIIIb**, mp 193–194°C.

^{1}H NMR spectrum of pyrrole **VIIb** ($CDCl_3$, δ, ppm): 1.77 m (4H, $C^{5,6}H_2$), 2.55 m (4H, $C^{4,7}H_2$), 7.09 s (1H, H^3), 7.25 d.d (1H, SCH=, *J* 9.3 Hz), 7.53 m (3H, H arom), 8.00 m (2H, H arom), 8.93 d.d (1H, COCH=, *J* 9.3 Hz). IR spectrum of pyrrole **VIIIb**, ν, cm^{-1}: 690, 740, 745, 766, 811, 827, 940, 1046, 1113, 1141, 1159, 1184, 1261, 1224, 1245, 1305, 1332, 1338, 1401, 1450, 1470, 1498, 1542, 1579, 1595, 1673, 2851, 2928. ^{1}H NMR spectrum of pyrrole **VIIIb** ($CDCl_3$, δ, ppm): 2.63 m (4H, $C^{4,7}H_2$), 1.82 m (4H, $C^{5,6}H_2$), 3.76 d.d (1H, $CHC\underline{H}_2$, *J* 10.3, 20 Hz), 3.98 d.d (1H, $CHC\underline{H}_2$, *J* 4.1, 20 Hz), 6.09 d.d (1H, $C\underline{H}CH_2$, *J* 4.1, 10.3 Hz), 6.73 s (1H, H^3), 7.52 m (3H, H arom), 7.91 m (2H, H arom). Found, %: C 65.84; H 5.35; N 4.56; S 19.85. $C_{18}H_{17}NOS_2$. Calculated, %: C 66.02; H 5.23; N 4.28; S 19.58.

2-(1-Thioxo-3-phenyl-5,6,7,8-tetrahydro-1*H*-[1,3]-thiasolo[3,4-a]indol-3-yl)-1-(2-furyl)ethan-1-one (VIIIe). Along procedure a described under compound **IIIa** from 0.12 g (1 mmol) of 4,5,6,7-tetrahydroindole, 0.06 g (1 mmol) of KOH, 0.15 g (2 mmol) of carbon disulfide, and 0.20 g (1 mmol) of acetylene was obtained 0.18 g (46%) of pyrrole **VIIIe**, mp 158–159°C. IR spectrum, ν, cm^{-1}: 553, 578, 592, 630, 665, 694, 711, 762, 812, 825, 882, 903, 953, 978, 1015, 1033, 1049, 1084, 1144, 1184, 1214, 1260, 1306, 1363, 1386, 1448, 1465, 1547, 1567, 1632, 1671, 2851, 2922, 3025, 3059, 3122. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.82 m (4H, $C^{5,6}H_2$), 2.63 m (4H, $C^{4,7}H_2$), 3.89, 4.2 d.d (2H, CH_2CO), 6.59 d.d (1H, H^4 of furan ring), 6.75 s (1H, H^3), 7.18 d.d (1H, H^3 of furan ring), 7.29 m (3H, H arom), 7.35 m (2H, H arom), 7.59 d.d (1H, H^5 of furan ring). Found, %: C 66.84; H 5.35; N 3.96; S 16.85. $C_{22}H_{19}NO_2S_2$. Calculated, %: C 67.15; H 4.87; N 3.56; S 16.30.

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