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Cyanoacetylene and Its Derivatives: XXVIII.[*] Reactions of 2-Mercaptobenzothiazole with Nitriles of α,β-Acetylene γ-Hydroxyacids and with 3-Phenyl-2-propynonitrile[**]

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Abstract—Nucleophilic addition of 2-mercaptobenzothiazole to 4-alkyl-4-hydroxy-2-alkynonitriles at 1 : 1 ratio in the presence of 4–6 wt% of Et_3N occurs regio- and stereospecifically to afford (*Z*)-4-alkyl-3-(benzothiazolyl-2-thio)-4-hydroxy-2-alkenonitriles (yield 40–51%). In the presence of 1.3 wt% of Dabco the thiazole and 4-hydroxy-4-methyl-2-pentynonitrile (1 : 1) give rise to a mixture of 2-alkenonitrile and 2-(3,3,6,6-tetramethyl-2-cyanomethyl-5-cyanomethylene-1,4-oxathian-2-yl)thiobenzothiazole. At the use of 4–6 wt% of LiOH arises an intractable mixture containing 1,4-oxathiane, benzothiazol-2-one, 2-[1-(5,5-dimethyl-2-cyanomethyl)-4-cyanomethylene-1,3-oxathiolan-2-yl)-1-methylethyl]thiobenzothiazole, bis(2,2,5,5-tetramethyl-6-cyanomethyl-3-cyanomethylene-1,4-oxathian-6-yl) disulfide, bis[1-(5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-oxathiolan-2-yl)-1-methylethyl] disulfide, and 3-[1-(5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-oxathiolan-2-yl)-1-methylethyl]benzothiazol-2-one (according to ^1H and ^{13}C NMR data). 2-mercaptobenzothiazole adds to 3-phenyl-2-propynonitrile in the presence of 7 wt% of KOH with *regio*- and stereospecific formation of (*Z*)-3-(benzothiazolyl-2-thio)-3-phenyl-2-propenonitrile (88%).

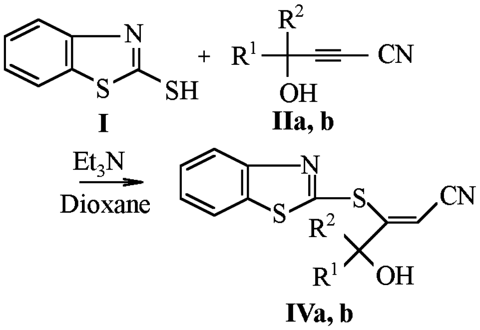
The reactivity of nitriles of α,β-acetylene γ-hydroxyacids toward O-, N-, and S-centered nucleophiles was treated in reviews [2, 3].

There are few data on reactions between acetylene compounds and 2-mercaptobenzothiazole (**I**) [4–6]. Acetylene reacts with thiazole **I** under stringent conditions (25 at, KOH, 170–175°C, 2h, dioxane) affording 1,3-benzothiazolyl 2-vinyl sulfide (yield 69%) [4]. A similar reaction carried out in 28–37% water solution of potassium hydroxide (12–14 at, molar ratio KOH : thiazole **I** 3.3 : 1, 130–200°C, 6–10 h) resulted in 2-aminophenyl vinyl sulfide in up to 98% yield [5]. Activated acetylenes, in particular, propiolic acid and its esters, and also acetylenedicarboxylic acid react with thiazole **I** (75–80°C, 2.5 h, ethanol) to furnish the corresponding derivatives of β-(2-benzothiazolylthio)acrylic and β-(2-benzothiazolylthio)fumaric acids [6].

The present study concerned addition of 2-mercaptobenzothiazole (**I**) to 4-alkyl-4-hydroxy-2-alkynonitriles (**IIa, b**) and to 3-phenyl-3-propynonitrile (**III**) with the aim to get new data on the effect of the addends and acetylenes structure on the reaction direction and to prepare new functionalized heterocyclic compounds interesting as probable pharmaceuticals.

The experiments showed that the direction of the reaction between thiazole **I** and 2-alkynonitriles **IIa, b** was considerably affected by the character of catalyst {triethylamine, 1,4-diazabicyclo[2.2.2]octane (Dabco), LiOH}, of solvent, and by the ratio of the initial reagents. The reaction does not occur without catalyst (20–25°C, 9 h, dioxane). In the presence of

Scheme 1.



$R^1 = R^2 =$ Me (**a**); R^1, $R^2 = (CH_2)_5$ (**b**).

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Et_3N (4–6 wt%, 20–25°C, 15 h, dioxane) equimolar amounts of thiazole **I** and acetylenes **IIa, b** react regio- and stereospecifically to afford (*Z*)-4-alkyl-3-(benzothiazolyl-2-thio)-4-hydroxy-2-alkenonitriles (**IVa, b**) in 40 and 51% yield respectively (Scheme 1).

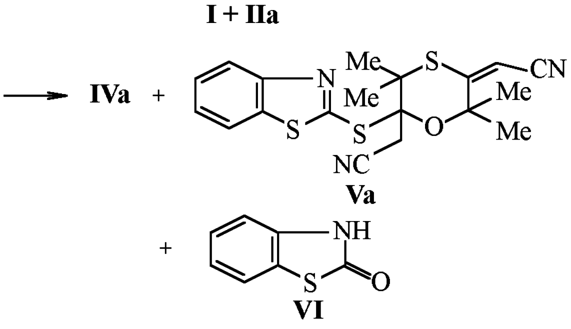
(*Z*)-3-(Benzothiazolyl-2-thio)-4-hydroxy-4-methyl-2-pentenonitrile (**IVa**) is crystalline, **IVb** is oily substance. The compounds are soluble in the most organic solvents. Their IR spectra contain absorption bands at 3437–3300 (OH), 3056–3040 (C=CH), 2212–2210 (=CH–CN), 1593–1580 (C=C) cm^{-1}.

In the ^1H NMR spectra ($CDCl_3$) of compounds **IVa, b** appear signals of olefin protons in 6.38 and 6.43 ppm regions respectively.

At another way of reagents mixing, i.e. at slow addition of 2-mercaptothiazole **I** to equimolar amount of acetylene **IIa** (6 wt% of ET_3N, 20–25°C, 10 h, dioxane) occurred considerable tarring, and we failed to separate the reaction products by column chromatography. Thiazole **I** conversion in this case was only 33%.

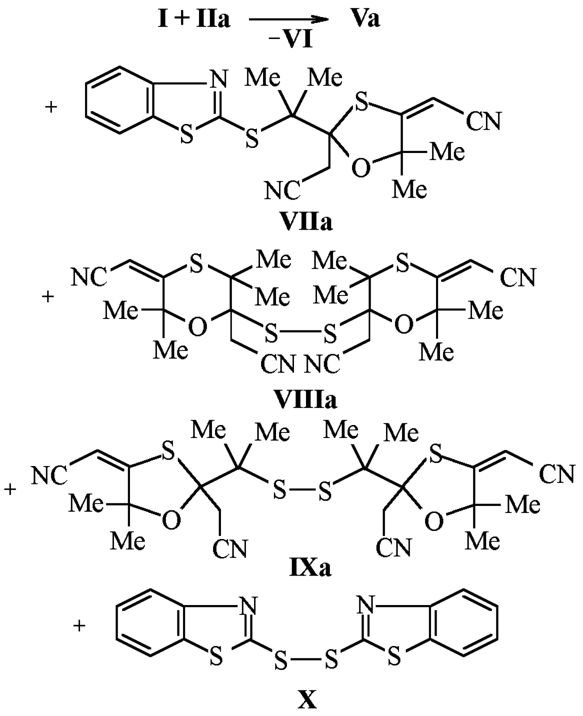
The reaction of 2-mercaptothiazole **I** with 4-hydroxy-4-methyl-2-pentynonitrile (**IIa**) at 1 : 1 ratio in the presence of 1.3 wt% of Dabco (dioxane, 20–25°C, 17 h) gave rise to products mixture composed of 2-pentenonitrile **IVa** and 2-(3,3,6,6-tetramethyl-2-cyanomethyl-5-cyanomethylene-1,4-oxathian-2-yl)thiobenzothiazole (**Va**) in 1 : 6 ratio (^1H NMR). Besides from the reaction mixture was isolated benzothiazol-2-one (**VI**) (Scheme 2).

Scheme 2.



If as catalyst served 6 wt% of LiOH (at equimolar ratio of reagents, 20–25°C, 4–10 h) both in dioxane and in acetonitrile the reaction did not stop at formation of addition products **IVa** or 1,4-oxathiane **Va**. As show ^1H NMR data the reaction results in a mixture of 1,4-oxathiane **Va**, 1,3-oxathiolane **VIIa**, bis(2,2,5,5-tetramethyl-6-cyanomethyl-3-cyanomethylene-1,4-oxathian-6-yl) disulfide (**VIIIa**), bis-[1-(5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-oxathiolan-2-yl)-1-methylethyl] disulfide (**IXa**), di(benzothiasol-2-yl) disulfide (**X**), and benzothiazol-2-one (**VI**) (Scheme 3).

Scheme 3.



Chemical shifts in ^{13}C NMR spectra of compounds **Va**–**X** are given in the table.

In the ^1H NMR spectrum of the mixture obtained are present four singlets at 5.26, 5.24, 5.14, and 5.10 ppm that may be attributed both to structures **V**–**IX** and to *E*- and *Z*-isomers of 1,4-oxathiane **Va** and 1,3-oxathiolane **VIIa**. However with the help of two-dimensional ^1H NMR spectroscopy (NOESY) we established that the compounds obtained were *E*-isomers as evidenced the cross-peaks of olefin protons and protons of methyl groups.

We failed to separate compounds **Ve** and **VIIa** by column chromatography or fractional crystallization.

Our numerous attempts to direct the process to production of a single product among the three substances shown in Scheme 3 did not succeed. For instance, at twofold excess of acetylene **IIa** with respect to thiazole **I** (4 wt% of LiOH, 20–25°C, 4 h, dioxane) the reaction finished in formation of a mixture of products (TLC monitoring). We isolated from

Chemical shifts in ^{13}C NMR spectra of compounds **Va, VI, VIIa–IXa, X, XIa**[a]

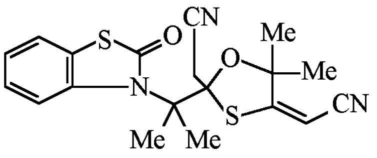
Compd. no.	Chemical shift, δ, ppm[b]														
	C^2	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}	C^{16}	C^{17}
Va	169.21	126.07	121.21	125.96	124.97	137.24	153.56	65.40	84.92	29.11	116.94	71.96	173.11	89.06	116.14
VI	173.14	111.90	126.59	122.58	123.32	124.11	135.63								
VIIa	168.75	126.07	121.22	123.27	121.48	131.95	149.34	84.78	100.86	32.10	117.49	94.86	171.10	84.95	116.51
VIIIa								66.85	92.01	[c]	117.44	74.24	173.25	89.20	116.94
IXa								90.50	103.19	[c]	117.01	95.00	171.22	84.78	116.51
X	160.23	126.07	121.50	123.28	121.11	135.23	152.90								
XIa	172.30	113.10	[c]	[c]	[c]	[c]	[c]	107.20	104.82	[c]	[c]	94.98	171.05	84.35	[c]

[a] Assignment of signals was performed basing on the data from [13].

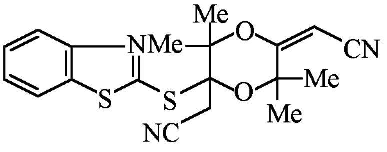
[b] Chemical shifts of atoms C^{18}–C^{21} in compounds **Va, VIIa–IXa, XIa** appear in the region 20–30 ppm.

[c] Chemical shift of atom C^{12} appears in 30 ppm region, those of C^{13} and C^{17} at 115–118 ppm and C^4–C^6 at 120–140 ppm.

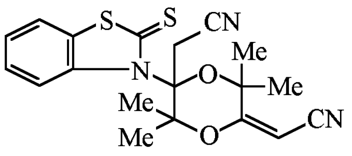
the mixture by column chromatography a yellow oily substance whose IR spectrum contained absorption bands with the frequencies 3040 cm^{-1} ($\mathrm{C{=}\underline{C}H}$), 2245 cm^{-1} ($\mathrm{CH_2\underline{C}N}$), 2210 cm^{-1} ($\mathrm{{=}CH\underline{C}N}$), 1765 cm^{-1} (C=O), 1660 and 1593 cm^{-1} (C=C), and no absorption band of hydroxy group. The elemental analysis corresponded to a formula $C_{19}H_{19}N_3O_2S_2$ that is consistent with several alternative structures **XIa–XIII**:



XIa



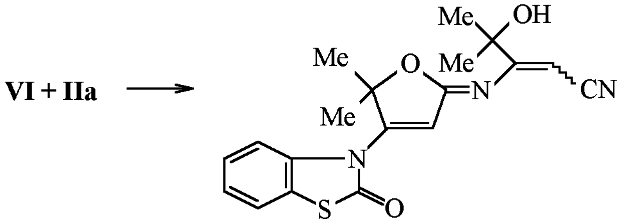
XII



XIII

In the ^{13}C NMR spectrum of the reaction mixture alongside the resonances belonging to the above mentioned substances **Va–X** (Scheme 3) arose a number of new signals at 84.35, 94.98, 104.82, 107.20, 113.10, 171.05 and 172.30 ppm. These signals correspond to 1,3-oxathiolane **XIa**, a product of nucleophilic addition to acetylene **IIa** of benzothiazol-2-one (**VI**) that formed in the course of the reaction (Scheme 2). The formation of a C–N bond in addition of benzothiazol-2-one to acetylene **IIa** is evidenced by downfield shift of 22 ppm of the signal from the atom C^{10} in 1,3-oxathiolane **XIa** as compared with 1,3-oxathiolane **VIIa** (see table).

Note that formerly [7] in reaction of benzothiazol-2-one with acetylene **IIa** in aprotic solvents (DMSO, acetonitrile, dioxane) at 20°C in the presence of LiOH (or KOH) was obtained another compound: 3-[5,5-dimethyl-4-(2-oxo-2,3-dihydro-1,3-benzothiazol-3-yl)-2,5-dihydro-2-furanylideneamino]-4-hydroxy-4-methyl-2-pentenonitrile (**XIV**).

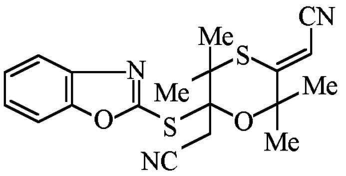


XIV

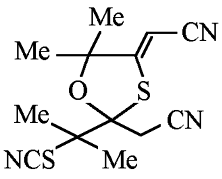
In ethanol (6 wt% of Et_3N, 20–25°C, 12 h) the reaction of thiazole **I** with acetylene **IIa** also gives rise to an intractable mixture of compounds **Va, VIIa–IXa**. In the IR spectrum of the mixture appear the absorption bands with the frequencies 3052 cm^{-1} ($\mathrm{C{=}\underline{C}H}$), 2249 cm^{-1} ($\mathrm{CH_2{-}\underline{C}N}$), 2214 cm^{-1} ($\mathrm{{=}CH{-}\underline{C}N}$), 1597 cm^{-1} (C=C), and the absorption bands of the hydroxy group are lacking.

We already observed before the formation of similar structures: The reaction of benzoxazole-2-

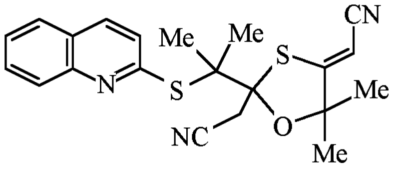
thione with acetylene **IIa** gave rise to 2-(3,3,6,6-tetramethyl-2-cyanomethyl-5-cyanomethylene-1,4-oxathian-2-yl)thiobenzoxazole (**XV**) [8], and 5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-oxathiolan-2-yl-1-methylethyl thiocyanate (**XVI**) was isolated in reaction of acetylene **II** with thiocyanic acid and its salts [9]. Besides in reaction of 2-mercaptoquinoline with acetylene **IIa** formed a mixture of structural isomers: 2-[1-(5,5-dimethyl-2-cyanomethyl)-4-cyanomethylene-1,3-oxathiolan-2-yl)-1-methylethyl]thioquinoline (**XVII**), and 2-(3,3,6,6-tetramethyl-2-cyanomethyl-5-cyanomethylene-1,4-oxathian-2-yl)thioquinoline (**XVIII**) in 3:5 ratio according to ^{1}H NMR data [10].

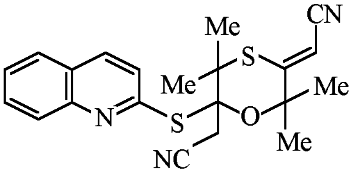


XV



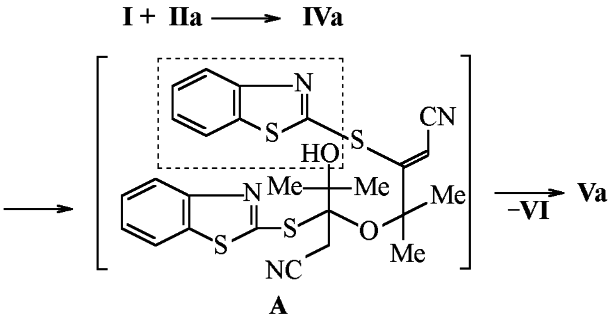
XVI





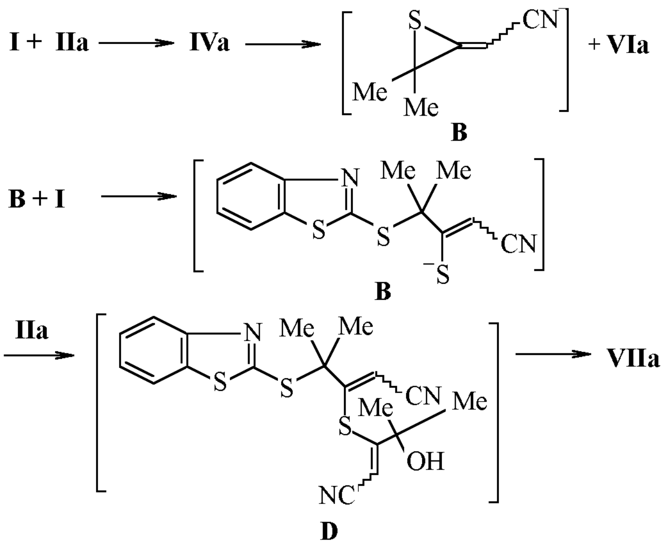
Apparently in the first stage thiazole **I** adds to the β-carbon of the triple bond in acetylene **IIa** giving the expected cyanoethenyl sulfide **IV** that then undergoes dimerization into intermediate **A**. The latter via intramolecular processes eliminates benzothiazol-2-one (**VI**) and transforms into 1,4-oxathiane (**Va**) (Scheme 4).

Scheme 4.



The reaction sequence resulting in 1,3-oxathiolane **VIIa** apparently also includes the formation of cyanoethenyl sulfide **IVa** that decomposes with liberation of benzothiazol-2-one (**VI**) and thiirane **B** (Scheme 5).

Scheme 5.



Thiirane **B** reacts with another molecule of 2-mercaptobenzothiazole (**I**) to give intermediate **C** that adds to the second molecule of acetylene **IIa** affording intermediate **D**. The latter further undergoes intramolecular cyclization via nucleophilic addition of hydroxy group to the electrophilic double bond to provide 1,3-oxathiolane **VIIa**.

In a similar way occurs a reaction between acetylene **IIa** and benzothiazol-2-one (**VI**) arising in the course of the process.

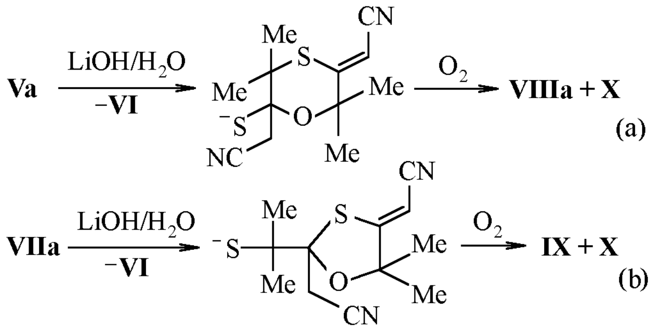
The formation of disulfides **VIIIa–X** may be represented as a result of a nucleophilic attack of hydroxide-ion on the "thioamide" carbon in *2* position of the benzothiazole moiety both in 1,4-oxathiane **Va** and in 1,3-oxathiolane **VIIa**. Further the thiolate-anions are oxidized with the air oxygen into thiinyl radicals that on dimerization afford disulfides **VIIIa–X** (Scheme 6, *a* and *b*).

A similar cleavage of C–S bond in 3-hydroxy-2-(2-hydroxyethylthio)-3,3-dialkyl-2-alkenonitriles was formerly observed [11] to occur under mild conditions (triethylamine or LiOH, 50°C or at storage in air for 50 days).

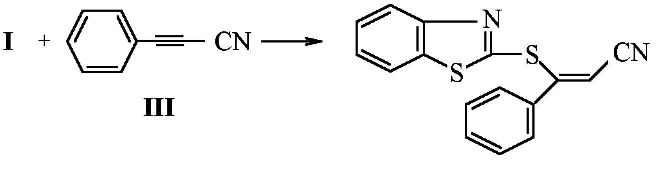
Thiazole **I** and 3-phenyl-2propynonitrile (**III**) react (7 wt% KOH, 20–25°C, 9 h, dioxane) regio- and stereospecifically to afford (*Z*)-3-(benzothiazolyl-2-

thio)-3-phenyl-2-propenonitrile (**XIX**) in 88% yield (Scheme 7).

Scheme 6.



Scheme 7.



XIX

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 in CDCl$_3$, internal reference HMDS. IR spectra were recorded on spectrometers Specord 75 IR and Bruker JFS-25 from thin film or KBr pellets. Mass spectra were measured on LKB-2091 instrument equipped with direct input system, ionizing electrons energy 58 eV. The reaction progress was monitored by TLC on Al$_2$O$_3$ and Silufol plates (eluent chloroform–benzene–ethanol, 20 : 4 : 1).

The initial acetylenes **IIa, b** and **III** were prepared by procedure [12]. 2-Mercaptobenzothiazole was purified as described in [13].

Reaction of 2-mercaptobenzothiazole (I) with 4-alkyl-4-hydroxy-2-alkynonitriles IIa, b. (a) To a mixture of 0.42 g (2.5 mmol) of 2-mercaptobenzothiazole (**I**), 0.04 g of Et$_3$N, and 10 ml of dioxane was slowly added 0.27 g (2.5 mmol) of acetylene **IIa** in 5 ml of dioxane, and the mixture was stirred for 15 h at 20–25°C. The solvent was removed in a vacuum, the residue was washed with ethyl ether and dried in a vacuum. We obtained 0.35 g (51%) of 3-(benzothiazolyl-2-thio)-4-hydroxy-4-methyl-2-pentenonitrile (**IVa**), mp 104–106°C. IR spectrum (ν, cm^{-1}): 3350–3300, 3040, 2970, 2930, 2850, 2210, 1630, 1580, 1450, 1410, 1360, 1350, 1305, 1190, 1130, 1070, 1010, 1000, 970, 820, 810, 750, 660, 595, 560. ^{1}H NMR spectrum (CDCl$_3$, δ, ppm): 1.56 s (6H, 2CH$_3$), 6.38 s (1H, =CH), 7.39–7.86 m (4H arom). Found, %: C 56.21; H 4.03; N 9.36; S 23.64. $C_{13}H_{12}N_2OS_2$. Calculated, %: C 56.50; H 4.38; N 10.14; S 23.20.

In a similar way from 0.13 g (0.8 mmol) of 2-mercaptobenzothiazole (**I**), 0.12 g (0.8 mmol) of acetylene **IIb** and 0.01 g Et$_3$N in 10 ml of dioxane was obtained 0.24 g of light-yellow substance. It was subjected to column chromatography on Al$_2$O$_3$ to isolate 0.1 g (40%) of 3-(benzothiazolyl-2-thio)-3-(1-hydroxy-1-cyclohexyl)-2-propenonitrile (**IVb**). IR spectrum (ν, cm^{-1}): 3437, 3056, 2932, 2855, 2212, 1666, 1593, 1466, 1447, 1343, 1306, 1271, 1215, 1124, 1071, 1017, 972, 929, 744, 705, 642. ^{1}H NMR spectrum (CDCl$_3$, δ, ppm): 1.65 br.s (10H, CH$_2$), 6.43 s (1H, =CH), 7.36–7.79 m (4H arom). Found, %: C 60.73; H 5.10; N 8.85; S 20.27. $C_{16}H_{16}N_2OS_2$. Calculated, %: C 59.77; H 5.46; N 8.14; S 20.12.

(b) To a mixture of 0.42 g (2.5 mmol) of 2-mercaptobenzothiazole (**I**), 0.009 g of Dabco, and 10 ml of dioxane was slowly added 0.27 g (2.5 mmol) of acetylene **IIa** in 5 ml of dioxane, and the mixture was stirred for 17 h at 20–25°C. The solvent was removed in a vacuum, the residue was washed with ethyl ether and dried in a vacuum. We obtained 0.68 g (51%) of light-yellow substance that was subjected to column chromatography on Al$_2$O$_3$ to isolate 0.04 g (17%) of compound **IVa** and 0.22 g (67%) of 2-(3,3,6,6-tetramethyl-2-cyanomethyl-5-cyanomethylene-1,4-oxathian-2-yl)thiobenzothiazole (**Va**). IR spectrum (ν, cm^{-1}): 3050, 2970, 2925, 2850, 2250, 2210, 1620, 1570, 1530, 1450, 1440, 1380, 1360, 1300, 1250, 1230, 1200, 1170, 1120, 1070, 1060, 1010, 970, 880, 870, 795, 750, 730, 670, 650, 570. ^{1}H NMR spectrum (δ, ppm): 1.75, 1.85, 1.93 s and 2.04 s (12H, 4CH$_3$), 3.76 d (2H, CH$_2$), 5.24 s (1H, =CH), 7.29–8.03 m (4H arom). Found, %: C 56.14; H 5.10; N 9.10; S 22.52. $C_{19}H_{19}N_3OS_3$. Calculated, %: C 56.83; H 4.77; N 10.46; S 23.96. Besides was separated 0.19 g (100%) of benzothiazol-2-one (**VI**), mp 136–138°C [14].

(c) To a mixture of 0.42 g (2.5 mmol) of 2-mercaptobenzothiazole (**I**), 0.04 g of LiOH, and 10 ml of dioxane was slowly added 0.27 g (2.5 mmol) of acetylene **IIa** in 5 ml of dioxane, and the mixture was stirred for 4 h at 20–25°C. The reaction mixture was passed through a 3 cm layer of Al$_2$O$_3$ on a glass frit. The solvent was removed in a vacuum, the residue was washed with ethyl ether, and dried in a vacuum. We obtained 0.68 g of crude product of yellow color containing compounds **Va**–**X** [^{1}H NMR spectrum (δ, ppm): 5.26 s, 5.24 s, 5.14 s, 5.10 s (=CH) and ^{13}C NMR spectrum (see table)]. By column chromatography of the mixture on Al_2O_3 was separated 0.39 g (78%) of a mixture of compounds **Va** and **VIIa** (in 1:1 ratio according to ^{1}H NMR data). IR spectrum (ν, cm^{-1}): 3052, 2970, 2928, 2858, 2250, 2215, 1598, 1534, 1458, 1442, 1386, 1367, 1311, 1252, 1237, 1204, 1125, 1060, 1016, 982, 874, 760, 729, 657, 587. ^{1}H NMR spectrum (δ, ppm): 1.4–2.0 (CH_3), 3.2–3.8 (CH_2), 5.14 s and 5.24 s (=CH), 7.04 – 8.05 m (H arom). Found, %: C 56.97; H 4.60; N 10.20; S 24.32. $C_{19}H_{19}N_3OS_3$. Calculated, %: C 56.83; H 4.77; N 10.46; S 23.96. Besides was separated 0.17 g of benzothiazol-2-one (**VI**).

(d) To a mixture of 0.33 g (2 mmol) of 2-mercaptobenzothiazole (**I**), 0.03 g of LiOH, and 5 ml of acetonitrile was added 0.22 g (2 mmol) of acetylene **IIa** in 5 ml of acetonitrile, and the mixture was stirred for 10 h at 20–25°C. The reaction mixture was passed through a 3 cm layer of Al_2O_3 on a glass frit. The solvent was removed in a vacuum, and from the residue was separated by column chromatography on Al_2O_3 0.03 g of benzothiazol-2-one (**VI**) and 0.2 g of a mixture of compounds **Va, VIIa–X** [^{1}H NMR spectrum (δ, ppm): 5.26 s, 5.24 s, 5.14 s, 5.10 s (=CH)].

(e) To a mixture of 0.42 g (2.5 mmol) of 2-mercaptobenzothiazole (**I**), 0.04 g of LiOH, and 10 ml of dioxane was slowly added 0.54 g (5 mmol) of acetylene **IIa** in 5 ml of dioxane, and the mixture was stirred for 4 h at 20–25°C. The reaction mixture was passed through a 3 cm layer of Al_2O_3 on a glass frit. The solvent was removed in a vacuum, the residue was washed with ethyl ether, and dried in a vacuum. We obtained 1 g of yellow product containing compounds **Va–XIa** (^{1}H NMR spectrum see table). By chromatography on silica gel were isolated 0.35 g (70%) of the mixture of compounds **Va** and **VIIa** (in 1:3 ratio according to ^{1}H NMR data), 0.06 g (12%) of compound **XIa**, and 0.14 g of benzothiazol-2-one. IR spectrum of compound **XIa** (ν, cm^{-1}): 3040, 2970, 2940, 2850, 2245, 2205, 1765, 1660, 1593, 1525, 1450, 1440, 1380, 1360, 1300, 1280, 1250, 1240, 1200, 1140, 1110, 1060, 1010, 980, 950, 900, 880, 870, 830, 800, 760, 730, 680, 640, 600, 570. Found, %: C 59.60; H 4.45; N 10.15; S 16.49. $C_{19}H_{19}N_3O_2S_2$. Calculated, %: C 59.20; H 4.97; N 10.90; S 16.64.

(f) To a mixture of 0.27 g (2.5 mmol) of acetylene **IIa**, 0.04 g of Et_3N, and 5 ml of dioxane was slowly added a solution of 0.42 g (2.5 mmol) of 2-mercaptobenzothiazole (**I**) in 10 ml of dioxane, and the mixture was stirred for 10 h at 20–25°C. The solvent was removed in a vacuum, the residue was dried in a vacuum. We obtained 0.69 g of light-yellow powder that was subjected to column chromatography on Al_2O_3 to afford 0.28 g of thiazole **I**, mp 182°C [13], conversion 33%.

3-Phenyl-3-(benzothiazol-2-thio)-2-propenonitrile (XIX). To a mixture of 0.33 g (2 mmol) of 2-mercaptobenzothiazole (**I**), 0.04 g of KOH, and 5 ml of dioxane was slowly added 0.25 g (2 mmol) of 3-phenyl-2-propynonitrile (**III**) in 5 ml of dioxane. The mixture was stirred at room temperature for 9 h, and the solvent was removed in a vacuum. The residue was dissolved in acetone and passed through a 3 cm layer of Al_2O_3 on a glass frit. The solvent was removed. Yield of compound **XIX** 0.52 g (88%), mp 116–117°C (from ethanol). IR spectrum (ν, cm^{-1}): 3040, 2210, 1590, 1570, 1480, 1450, 1440, 1420, 1310, 1230, 1180, 1080, 1020, 990, 930, 905, 850, 760, 750, 720, 695, 680, 610, 560. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 5.94 s (1H, =CH), 7.20–7.92 m (H arom). Found, %: C 65.75; H 3.85; N 9.24; S 21.66. $C_{16}H_{10}N_2S_2$. Calculated, %: C 65.28; H 3.42; N 9.52; S 21.78.

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