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Heterocyclization of 2-(Propargylsulfanyl)-1,3-thiazole Derivatives by the Action of Halogens

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Abstract—Reactions of 2-(propargylsulfanyl)-5-methyl-1,3,4-thiadiazole, *N*-[5-(propargylsulfanyl)-1,3,4-thiadiazol-2-yl]benzamide, 2-(propargylsulfanyl)-1,3-benzothiazole, and 2-(propargylsulfanyl)-4,5-dihydro-1,3-thiazole with iodine involved annulation of the unsaturated substituent with formation of fused thiazole ring. 2(5)-(Propargylsulfanyl)-1,3,4-thiadiazole derivatives reacted with bromine to give mixtures of heterocyclization products and bromine adducts to the triple bond. The bromination of 2-(propargylsulfanyl)-4,5-dihydro-1,3-thiazole afforded only the bromine addition product to the triple bond.

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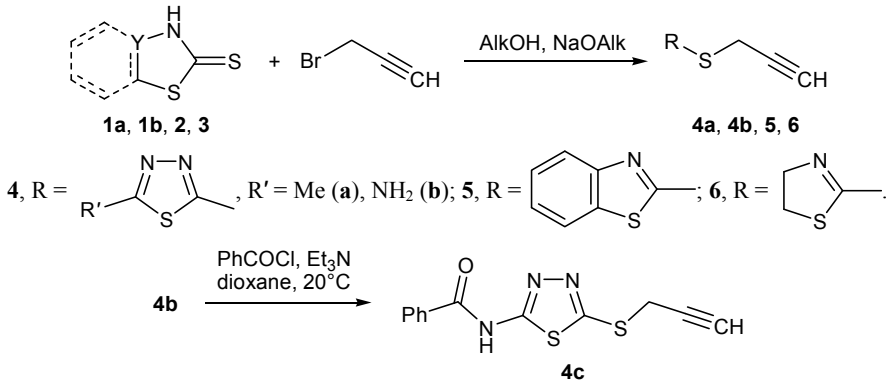
Synthesis and properties of fused thiazolo[2,3-*b*]-thiazolium and thiazolo[2,3-*b*][1,3,4]thiadiazolium systems attract much attention due to their efficiency as immune response modulators [1] and drugs for thrombolytic therapy [2]. The known procedure for the synthesis of these heterocyclic systems is based on heterocyclization of phenacylsulfanyl derivatives of 1,3-thiazole, dihydro-1,3-thiazole, and 1,3-benzothiazole. However, this procedure often requires fairly harsh conditions, in particular prolonged heating, and the use of concentrated mineral acids [1].

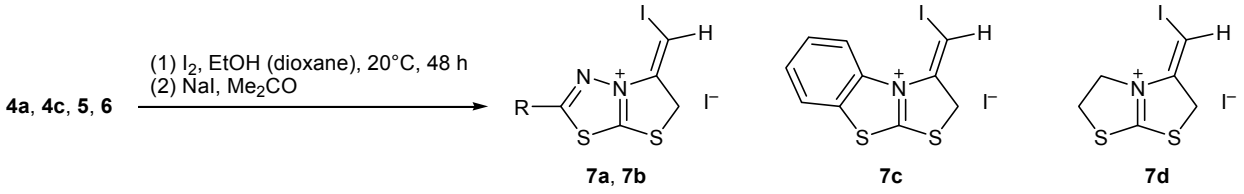
Dihydrothiazolo[2,3-*b*]thiazolium and dihydrothiazolo[2,3-*b*][1,3,4]thiadiazolium derivatives were synthesized previously [3−5] by halocyclization of 2-(alkenylsulfanyl)-1,3,4-thiadiazoles, -1,3-benzothiazoles, and -4,5-dihydro-1,3-thiazole at room temperature. In this work we have studied reactions of 2-(propargylsulfanyl)-1,3,4-thiadiazoles and -1,3-thiazoles with iodine and bromine with the goal of obtaining thiazolo-[2,3-*b*]thiazolium and thiazolo[2,3-*b*][1,3,4]thiadiazolium derivatives.

By reacting 5-methyl-1,3,4-thiadiazole-2-thione (**1a**), 5-amino-1,3,4-thiadiazole-2-thione (**1b**), 1,3-benzothiazole-2-thione (**2**), and 4,5-dihydro-1,3-thiazole-2-thione (**3**) with propargyl bromide in ethanol or propan-2-ol we obtained 2-methyl-5-(propargylsulfanyl)-1,3,4-thiadiazole (**4a**). 5-(propargylsulfanyl)-1,3,4-thiadiazol-2-amine (**4b**), 2-(propargylsulfanyl)-

Scheme 1.



Scheme 2.



R = Me (**a**), PhC(O)NH (**b**).

1,3-benzothiazole (**5**), and 2-(propargylsulfanyl)-4,5-dihydro-1,3-thiazole (**6**), respectively. The acylation of **4b** with benzoyl chloride afforded *N*-[5-(propargylsulfanyl)-1,3,4-thiadiazol-2-yl]benzamide (**4c**) (Scheme 1). In the ^{1}H NMR spectrum of all sulfides **4**–**6**, the most upfield signal due to CH≡ proton was located at δ 2.31–3.29 ppm. The mass spectra of all propargyl derivatives showed ion peaks resulting from elimination of the propargyl and propargylsulfanyl fragments from the molecular ion.

We were the first to study the reactions of compounds **4a** and **4c** with iodine. These reactions involved closure of 1,3-thiazole ring with formation of 5-(iodomethylidene)-2-methyl-5,6-dihydro[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazolium iodide (**7a**) and 2-benzoylamino-5-(iodomethylidene)-5,6-dihydro[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazolium iodide (**7b**), respectively (Scheme 2). The =CHI proton resonated in the ^{1}H NMR spectra of **7a** and **7b** at δ 7.40 and 7.20 ppm, respectively, and the =CHI carbon signal was observed in their ^{13}C NMR spectra at δ_C 71.8 and 70.6 ppm.

The configuration of the exocyclic C=C double bond in **7a** was determined using two-dimensional NMR experiment. The 6-H and =CHI signals in the ^{1}H NMR spectrum of **7a** were a doublet and a triplet, respectively, with a coupling constant *J* of 3 Hz, and the 2D ^{1}H–^{1}H NOESY spectrum of **7a** showed a correlation between these protons, which indicated their spatial proximity and hence *Z* configuration of the exocyclic double bond (Fig. 1).

Regioselective cyclization of 2-(propargylsulfanyl)-1,3-benzothiazole (**5**) by the action of iodine gave

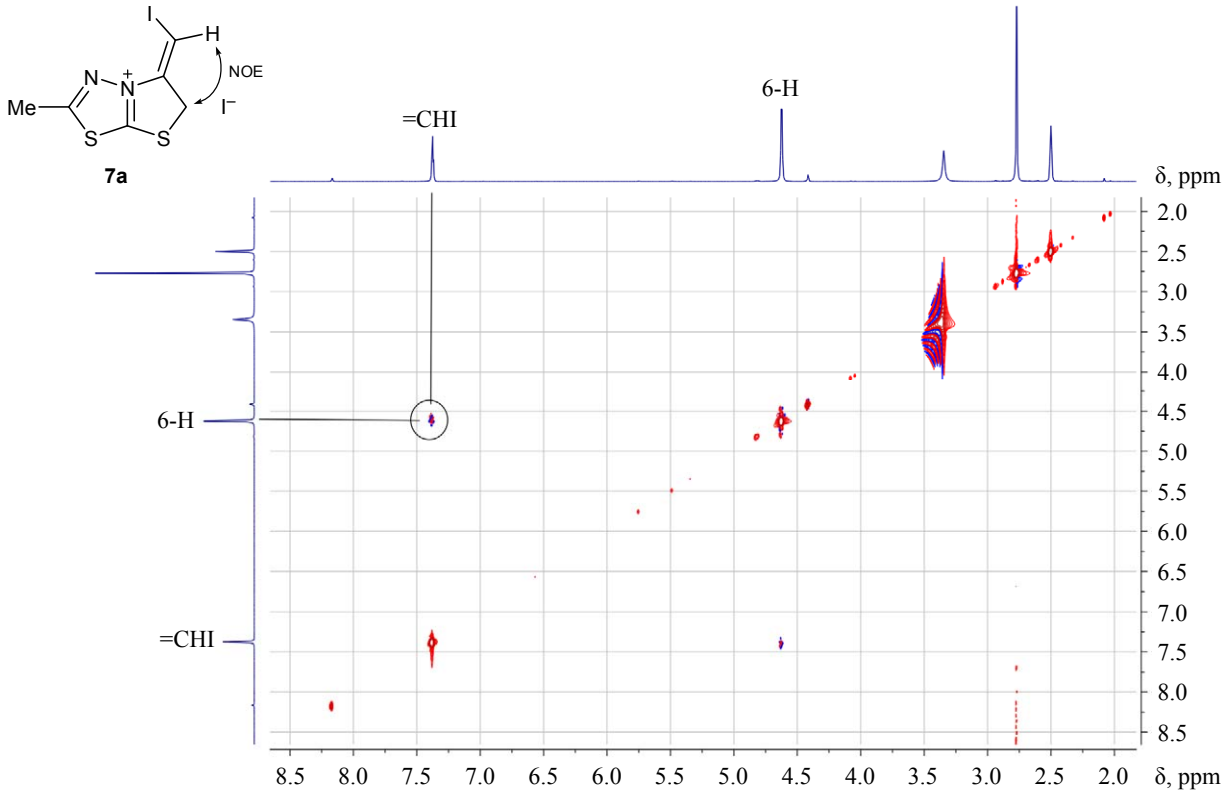
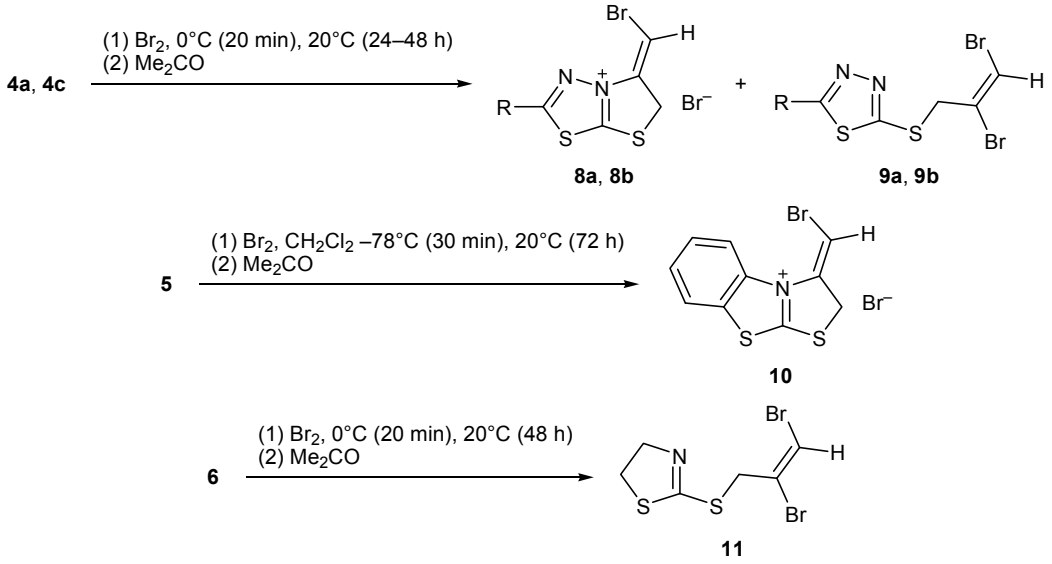


Fig. 1. ^{1}H–^{1}H NOESY spectrum of 5-(iodomethylidene)-2-methyl-5,6-dihydro[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazol-4-ium iodide (**7a**).

Scheme 3.



R = Me (**a**), PhC(O)NH (**b**).

3-(iodomethylidene)-2,3-dihydrobenzo[1,3]thiazolo-[2,3-*b*][1,3]benzothiazolium iodide (**7c**). The presence of a fused benzene ring induced downfield shift of all proton signals in the ^{1}H NMR spectrum of **7c** compared to **7a** and **7b**, and the =CHI signal of **7c** was located at δ 8.00 ppm. Likewise, 2-(propargylsulfanyl)-4,5-dihydro-1,3-thiazole (**6**) reacted with iodine to form 3-(iodomethylidene)-2,3,5,6-tetrahydro[1,3]-thiazolo[2,3-*b*][1,3]thiazolium iodide (**7d**) (Scheme 2).

The reactions of **4a**, **4c**, **5**, and **6** with bromine were less selective due to concurrent bromine addition to the triple bond. In the reaction with **4a**, the corresponding heterocyclization product, 5-(bromomethylidene)-2-methyl-5,6-dihydro[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazolium bromide (**8a**) was isolated in 38% yield. After separation of **8a**, the solution contained 2-(2,3-dibromoprop-2-en-1-ylsulfanyl)-5-methyl-1,3,4-thiadiazole (**9a**) which was identified by GC/MS. Compound **4c** reacted with bromine in dioxane to give a mixture of 2-benzamido-5-(bromomethylidene)-5,6-dihydro-[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazolium bromide (**8b**) and *N*-[5-(2,3-dibromoprop-2-en-1-ylsulfanyl)-1,3,4-thiadiazol-2-yl]benzamide (**9b**) at a ratio of 5:2 with an overall yield of 54%. Compound **8b** was also obtained in 36% yield by reaction of **4c** with bromine in methylene chloride (Scheme 3).

In the ^{1}H NMR spectrum of **9b**, the =CHBr proton resonated at δ 7.15 ppm, which is typical of analogous dibromoalkenes [6]. The =CHBr signal of **8b** was observed in a weaker field, at δ 7.24 ppm. The 6-H and =CHBr signals in the ^{1}H NMR spectra of **8a** and **8b** were a doublet and a triplet, respectively, due to long-range coupling with each other (as in the spectra of compounds **7a**–**7d**).

3-(Bromomethylidene)-2,3-dihydro[1,3]thiazolo-[2,3-*b*][1,3]benzothiazolium bromide (**10**) was obtained by reaction of sulfide **5** with bromine in methylene chloride on cooling to –78°C (Scheme 3). No heterocyclization product was formed when the reaction of **5** with bromine was carried out at 0°C.

The bromination of 2-(propargylsulfanyl)-4,5-dihydro-1,3-thiazole (**6**) in glacial acetic acid or in dioxane at 0°C afforded 2-(2,3-dibromoprop-2-en-1-ylsulfanyl)-4,5-dihydro-1,3-thiazole (**11**) (Scheme 3). As in the ^{1}H NMR spectra of bromine addition products **9a** and **9b**, the SCH_2 and =CHBr protons of **11** resonated as singlets. The reaction direction did not change when the reaction temperature was lowered to –78°C. Presumably, the nitrogen atom in the dihydrothiazole ring is more basic than in aromatic analogs and is efficiently solvated by solvent molecules, which makes it inaccessible for heterocyclization and favors electrophilic addition of bromine to the triple bond. The mass spectrum of **11** contained $[M - Br]^+$ ion peak with *m*/*z* 236/238 and $[CH_2CHBr{=}CHBr]^+$ ion peak with *m*/*z* 197/199/201.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker DRX-400 (400 MHz) and Bruker Avance 500 (500 MHz) spectrometers using tetramethylsilane as

internal standard. Two-dimensional ^1H–^1H NOESY experiments were carried out on a Bruker Avance II spectrometer (400 MHz, TMS). The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS QP-2010 Ultra instrument (ion peaks with a relative intensity of less than 5% were taken into account for key molecular fragments). The elemental compositions were determined with a Carlo Erba CHNS-O EA 1108 analyzer. The melting points were measured on a PTP (M) melting point apparatus. The solvents used were preliminarily distilled; ethanol was dried over CaO; dioxane was refluxed over alkali, dried, and distilled over metallic sodium.

Compounds 4a, 4b, 5, and 6 (*general procedure*). An equimolar amount of propargyl bromide was added to a solution of 8 mmol of compound **1a**, 16 mmol of **1b**, 40 mmol of **2**, or 10 mmol of **3** in 20 mL of ethanol or propan-2-ol, and the mixture was stirred for 12–20 h. The precipitate of NaBr was filtered off, and the filtrate was evaporated. In the synthesis of **4a**, **5**, and **6**, the residue was treated with diethyl ether (3 × 10 mL), the extracts were combined and filtered, and the filtrate was evaporated. Compound **4b** was isolated by recrystallization from propan-2-ol.

2-Methyl-5-(prop-2-yn-1-ylsulfanyl)-1,3,4-thiadiazole (4a). Yield 0.94 g (69%), yellow viscous liquid. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.31 t (1H, CH≡, J = 2.6 Hz), 2.76 s (3H, 2-CH_3), 4.04 d (2H, SCH_2, J = 2.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.5, 42.1, 99.6, 137.8, 172.7, 181.97. Mass spectrum, m/z (I_{rel}, %): 170 (16) $[M]^+$, 169 (<5) $[M - H]^+$, 137 (<5) $[M - SH]^+$, 131 (9) $[C_4H_5NS_2]^+$, 129 (100) $[C_4H_3NS_2]^+$, 128 (5), 102 (8), 96 (5), 90 (6), 85 (13), 76 (9), 73 (7), 72 (7), 71 (79) $[C_3H_3S]^+$, 70 (14), 69 (11), 59 (56) $[C_2H_3S]^+$, 58 (17), 45 (21) $[C_3H_3]^+$, 42 (5), 39 (45). Found, %: C 42.15; H 3.58; N 16.54. $C_6H_6N_2S_2$. Calculated, %: C 42.35; H 3.53; N 16.47.

5-(Prop-2-yn-1-ylsulfanyl)-1,3,4-thiadiazol-2-amine (4b). Yield 1.89 g (68%), white powder, mp 115–116°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.29 t (1H, ≡CH, J = 2.5 Hz), 3.89 d (2H, SCH_2, J = 2.5 Hz), 7.40 br.s (2H, NH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.3, 75.5, 80.1, 148.8, 170.9. Mass spectrum, m/z (I_{rel}, %): 171 (26) $[M]^+$, 170 (<5%) $[M - H]^+$, 132 (4) $[M - C_3H_3]^+$, 131 (9) $[M - C_3H_3 - H]^+$, 130 (7), 128 (100) $[C_4H_2NS_2]^+$, 102 (6), 85 (6), 74 (8), 71 (60) $[C_3H_3S]^+$, 70 (8), 69 (7), 60 (53), 59 (5), 45 (18) $[C_3H_3]^+$, 39 (50). Found, %: C 35.02; H 2.88; N 24.60. $C_5H_5N_3S_2$. Calculated, %: C 35.07; H 2.94; N 24.54.

***N*-[5-(Prop-2-yn-1-ylsulfanyl)-1,3,4-thiadiazol-2-yl]benzamide (4c).** Compound **4b**, 0.60 g (3.4 mmol), was dissolved in 10 mL of dioxane, 1.21 mL (3.4 mmol) of triethylamine and 0.58 mL (3.4 mmol) of benzoyl chloride were added, and the mixture was stirred for 12 h at room temperature. The precipitate was filtered off, the solvent was distilled off from the filtrate, and the residue was recrystallized from ethanol. Yield 0.49 g (52%), white solid, mp 198–200°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.36 t (1H, ≡CH, J = 2.5 Hz), 4.11 d (2H, SCH_2, J = 2.6 Hz), 7.55–7.60 m (2H, H_{arom}), 7.65–7.70 m (1H, H_{arom}), 8.12–8.15 m (2H, H_{arom}), 13.19 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 8.9, 22.6, 45.9, 75.6, 79.9, 128.9, 129.1, 131.7, 133.5, 157.9, 160.9, 165.7. Found, %: C 52.32; H 3.31; N 15.22. $C_{12}H_9N_3OS_2$. Calculated, %: C 52.34; H 3.29; N 15.26.

2-(Prop-2-yn-1-ylsulfanyl)-1,3-benzothiazole (5). Yield 4.71 g (55%), yellow viscous liquid. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.31 t (1H, ≡CH, J = 2.64 Hz), 4.26 (2H, SCH_2, J = 7.31 Hz), 7.39 (1H, H_{arom}), 7.49 m (1H, H_{arom}), 7.90 m (1H, H_{arom}), 8.06 m (1H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 205 (100) $[M]^+$, 204 (40) $[M - H]^+$, 173 (16) $[M - S]^+$, 172 (11) $[M - SH]^+$, 166 (23) $[M - C_3H_3]^+$, 161 (14) $[M - CS]^+$, 160 (11), 139 (5), 135 (7), 129 (20), 122 (17), 108 (37) $[C_6S]^{+\cdot}$, 102 (12), 82 (7), 71 (5), 70 (5), 69 (15), 63 (9), 45 (8), 39 (12). Found, %: C 58.48; H 3.51; N 6.79. $C_{10}H_7NS_2$. Calculated, %: C 58.50; H 3.44; N 6.82.

2-(Prop-2-yn-1-ylsulfanyl)-4,5-dihydro-1,3-thiazole (6). Yield 1.04 g (66%), yellow viscous liquid. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.26 t (1H, ≡CH, J = 2.65 Hz), 3.44 t (2H, 5-H, J = 7.98 Hz), 3.88 d (2H, SCH_2, J = 2.65 Hz), 4.24 t (2H, NCH_2, J = 7.98 Hz). Mass spectrum, m/z (I_{rel}, %): 157 (13) $[M]^{+\cdot}$, 156 (100) $[M - H]^+$, 131 (6) $[M - C_2H_2]^{+\cdot}$, 129 (54) $[M - C_2H_4]^{+\cdot}$, 124 (<5) $[M - SCH_3]^+$, 97 (5), 85 (15) $[M - C_3H_3S]^+$, 81 (15), 80 (16), 72 (52) $[C_3H_4S]^{+\cdot}$, 71 (28) $[C_3H_3S]^+$, 70 (10), 69 (10), 61 (7), 60 (59) $[SC_2H_4]^{+\cdot}$, 59 (48) $[SC_2H_3]^+$, 58 (14), 54 (11), 49 (10), 45 (43), 39 (30). Found, %: C 45.78; H 4.54; N 8.90. $C_6H_7NS_2$. Calculated, %: C 45.83; H 4.49; N 8.91.

Compounds 7a–7d (*general procedure*). A solution of 0.18 g (1 mmol) of compound **4a** in 5 mL of ethanol, or 0.2 g (0.7 mmol) of **4c** in 10 mL of dioxane, or 1 g (5 mmol) of **5** in 20 mL of ethanol, or 0.2 g (1 mmol) of **6** in 5 mL of ethanol was added to a solution of 2 equiv of iodine in 5 mL of ethanol or dioxane. The mixture was stirred for 24–72 h at room temperature, the solvent was evaporated, and the resi-

due was treated with excess sodium iodide in acetone. The yellow precipitate was filtered off and washed with 20 mL of acetone.

5-(Iodomethylidene)-2-methyl-5,6-dihydro[1,3]-thiazolo[2,3-*b*][1,3,4]thiadiazol-4-ium iodide (7a). Yield 0.25 g (59%), mp 197–199°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.78 s (3H, CH_3), 4.63 d (2H, 6-H, J = 3.0 Hz), 7.38 t (1H, =CHI, J = 2.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 17.5, 45.0, 71.8, 139.9, 172.5, 180.9. Found, %: C 16.95; H 1.49; N 6.62. $C_6H_6I_2N_2S_2$. Calculated, %: C 16.99; H 1.43; N 6.61.

2-Benzamido-5-(iodomethylidene)-5,6-dihydro-[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazol-4-ium iodide (7b). Yield 0.28 g (76%), mp 201–203°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.65 d (2H, 6-H, J = 3.1 Hz), 7.22 t (1H, =CHI, J = 3.1 Hz), 7.59 t (2H, H_{arom}, J = 6.4 Hz), 7.66–7.76 m (2H, H_{arom}), 8.13 d (1H, H_{arom}, J = 7.2 Hz), 13.20 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 43.9, 66.8, 70.6, 129.1, 129.3, 131.6, 132.2, 134.1, 140.9, 165.2, 168.9, 174.1. Found, %: C 27.19; H 1.74; N 7.92. $C_6H_6I_2N_2S_2$. Calculated, %: C 27.24; H 1.71; N 7.94.

3-(Iodomethylidene)-2,3-dihydro[1,3]thiazolo-[2,3-*b*][1,3]benzothiazol-4-ium iodide (7c). Yield 2.50 g (54%), mp 224–226°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.79 d (2H, 2-H, J = 2.9 Hz), 7.72 m (2H, H_{arom}), 8.00 t (1H, =CHI, J = 2.9 Hz), 8.39 d (1H, H_{arom}, J = 7.8 Hz), 8.53 d (1H, H_{arom}, J = 8.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 47.7, 66.8, 75.4, 115.9, 125.6, 127.2, 127.9, 129.6, 133.9, 140.6. Found, %: C 26.12; H 1.59; N 3.13. $C_{10}H_7I_2NS_2$. Calculated, %: C 26.16; H 1.54; N 3.05.

3-(Iodomethylidene)-2,3,5,6-tetrahydro[1,3]thiazolo[2,3-*b*][1,3]thiazol-4-ium iodide (7d). Yield 0.27 g (51%), mp 134–136°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.09 d.d (2H, 6-H, J = 9.5, 7.7 Hz), 4.29 d.d (2H, 5-H, J = 9.6, 7.7 Hz), 4.66 d (2H, 2-H, J = 2.9 Hz), 6.80 t (1H, =CHI, J = 2.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 37.8, 47.4, 50.3, 141.9, 196.1. Found, %: C 17.23; H 1.84; N 3.37. $C_6H_7I_2NS_2$. Calculated, %: C 17.53; H 1.72; N 3.41.

Bromination of compounds 4a, 4c, and 6 (*general procedure*). To a solution of 0.13 g (0.8 mmol) of compound **4a** in 20 mL of methylene chloride, or 0.25 g (0.9 mmol) of **4c** in 10 mL of dioxane, or 0.21 g (1 mmol) of **6** in 10 mL of glacial acetic acid (or dioxane) we added with stirring and cooling with ice a solution of 1.5 equiv of bromine in 5 mL of the same solvent over a period of 20 min. The mixture was stirred for 24–72 h at room temperature and was then treated as indicated below.

5-(Bromomethylidene)-2-methyl-5,6-dihydro-[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazol-4-ium bromide (8a). After 24 h, the solvent was removed, the residue was treated with acetone, and the white solid was filtered off and washed with 10 mL of acetone. Yield 0.1 g (38%), mp 298–300°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.78 s (3H, CH_3), 4.70 d (2H, 6-H, J = 3.3 Hz), 7.48 t (1H, =CHBr, J = 3.3 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 17.4, 42.0, 99.5, 137.8, 172.7, 181.9. Found, %: C 21.74; H 2.01; N 8.54. $C_6H_6Br_2N_2S_2$. Calculated, %: C 21.83; H 1.83; N 8.49.

2-(2,3-Dibromoprop-2-en-1-ylsulfanyl)-5-methyl-1,3,4-thiadiazole (9a). Mass spectrum (filtrate), m/z (I_{rel}, %): 251 (100) $[M - Br]^+$, 249 (99) $[M - Br]^+$, 201 (5) $[CH_2CHBr{=}CHBr]^+$, 199 (12) $[CH_2CHBr{=}CHBr]^+$, 197 (6) $[CH_2CHBr{=}CHBr]^+$, 175 (20), 173 (22), 172 (7), 171 (9), 170 (76), 149 (5), 133 (10), 132 (14), 129 (41), 119 (10), 117 (11), 107 (5), 105 (5), 102 (5), 99 (7), 97 (5), 87 (18), 85 (9), 83 (7), 73 (42), 71 (21), 70 (8), 61 (5), 60 (9), 59 (47), 58 (13), 57 (14), 56 (7).

2-Benzamido-5-(bromomethylidene)-5,6-dihydro[1,3]thiazolo[2,3-*b*][1,3,4]thiadiazolium bromide (8b) and *N*-[5-(2,3-dibromoprop-2-en-1-ylsulfanyl)-1,3,4-thiadiazol-2-yl]benzamide (9b). *a*. After 48 h, the solvent was removed, the residue was treated with acetone, and the yellow solid was filtered off and washed with 10 mL of acetone. The product, 0.21 g (54%), was a mixture of compounds **8b** and **9b**. A 0.1-g portion of that mixture was heated for 10 min in 5 mL of propan-2-ol under reflux; after cooling, the white solid (**8b**) was filtered off. Yield 0.03 g (25%), mp 188°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: **8b**: 4.73 d (2H, 6-H, J = 3.2 Hz), 7.24 t (1H, =CHBr, J = 3.2 Hz), 7.53–7.78 m (3H, H_{arom}), 8.13 t (2H, H_{arom}, J = 7.1 Hz), 13.18 br.s (1H, NH); **9b**: 4.37 d (2H, SCH_2, J = 3.2 Hz), 7.15 s (1H, CHBr), 7.53–7.78 m (3H, H_{arom}), 8.13 t (2H, H_{arom}, J = 7.1 Hz), 13.18 br.s (1H, NH).

Compound 8b. *b*. A solution of 0.02 mL (0.3 mmol) of bromine in 5 mL of methylene chloride was added over a period of 30 min with stirring and cooling with ice to a solution of 0.08 g (0.2 mmol) of compound **4c** in 10 mL of methylene chloride. After 10 days, the yellow solid was filtered off and washed on a filter with 10 mL of acetone. Yield 0.04 g (36%), mp 188°C (decomp.). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm:

40.5, 61.95, 98.3, 128.7, 128.8, 128.9, 130.59, 133.8, 138.1, 164.2, 167.99, 174.9. Found, %: C 33.10; H 2.11; N 9.71. $C_6H_7Br_2NS_2$. Calculated, %: C 33.12; H 2.08; N 9.66.

2-(2,3-Dibromoprop-2-en-1-ylsulfanyl)-4,5-dihydro-1,3-thiazole (11). *a*. After 48 h, the solvent was removed, the residue was treated with acetone, and the yellow solid was filtered off and washed with 10 mL of acetone. Yield 0.29 g (78%), mp 135–137°C.

b. Compound **11** was synthesized from 0.25 g (1.6 mmol) of sulfide **6** in 20 mL of dioxane. After 72 h, the yellow solid was filtered off and washed with dioxane (3 × 5 mL). Yield 0.43 g (84%), mp 135–136°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.53 t and (2H, 5-H, J = 8.1 Hz), 4.17 t (2H, 4-H, J = 8.1 Hz), 4.41 s (2H, SCH_2), 7.15 s (1H, =CHBr). Mass spectrum, m/z (I_{rel}, %): 238/236 (60/61) $[M - Br]^+$, 201/199/197 (63/100/86) $[CH_2CHBr{=}CHBr]^+$, 157 (9), 118 (15), 82 (14), 81 (6), 72 (19), 71 (6), 61 (6), 60 (23), 59 (14), 45 (10), 44 (5), 43 (7), 42 (5), 39 (11). Found, %: C 22.81; H 2.18; N 4.45. $C_6H_7Br_2NS_2$. Calculated, %: C 22.73; H 2.23; N 4.42.

3-(Bromomethylidene)-2,3-dihydro[1,3]thiazolo-[2,3-*b*][1,3]benzothiazol-4-ium bromide (10). A solution of 0.22 g (1.1 mmol) of compound **5** in 20 mL of methylene chloride was cooled to –78°C (dry ice–methanol bath), and a solution of 0.09 mL (1.65 mmol) of bromine in 5 mL of methylene chloride was added with stirring. The mixture was stirred for 2 h at –78°C and for 72 h at room temperature. The yellow solid was filtered off and washed with 10 mL of methylene chloride and acetone (3×10 mL). Yield 0.23 g (58%), mp 295–297°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.87 d (2H, 2-H, J = 2.8 Hz), 7.68–7.79 m (2H, H_{arom}), 8.04 t (1H, =CHBr, J = 2.8 Hz), 8.39 d.d (1H, H_{arom}, J = 1.1, 7.7 Hz), 8.49 d (1H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 44.2, 101.6, 116.1, 155.7, 127.9, 129.4, 130.9, 133.9, 135.9, 140.4. Found, %: C 32.89; H 2.12; N 3.80. $C_6H_7Br_2NS_2$. Calculated, %: C 32.90; H 1.93; N 3.84.

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