

Benzazoles: III.¹ Synthesis and Transformations of 6-(Chlorosulfonyl)-1,3-benzothiazol-2(3H)-ones

D. A. Dushamov^{a,*}, Yu. R. Takhirov^a, R. Sh. Kuryazov^a, and N. S. Mukhamedov^b

^a Urgench State University, Urgench, 220100 Uzbekistan

^b Yunusov Institute of the Chemistry of Plant Substances, Tashkent, 100170 Uzbekistan

*e-mail: dilshod.d71@mail.ru

Received May 18, 2020; revised June 1, 2020; accepted June 9, 2020

Abstract—Treatment of 1,3-benzothiazol-2(3H)-one and its 3-methyl derivative with chlorosulfonic acid afforded the corresponding 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonyl chlorides which reacted with water, alcohols, and amines to give 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonic acids and their esters and amides.

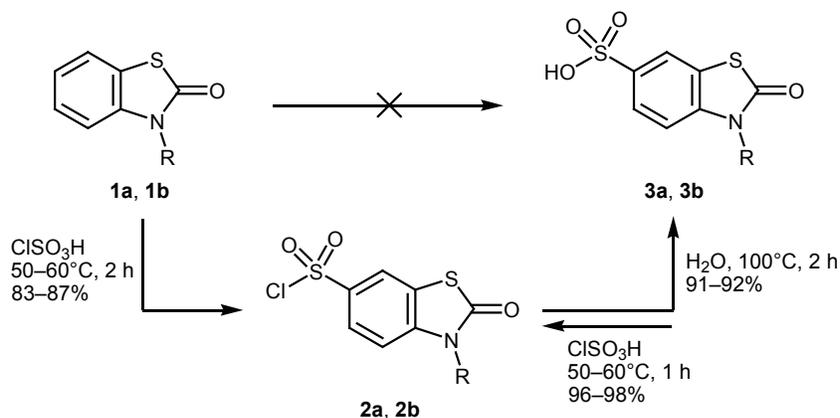
Keywords: 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonamides, 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonic acid esters, 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonic acids, 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonyl chlorides, electrophilic substitution, nucleophilic substitution

DOI: 10.1134/S1070428020090031

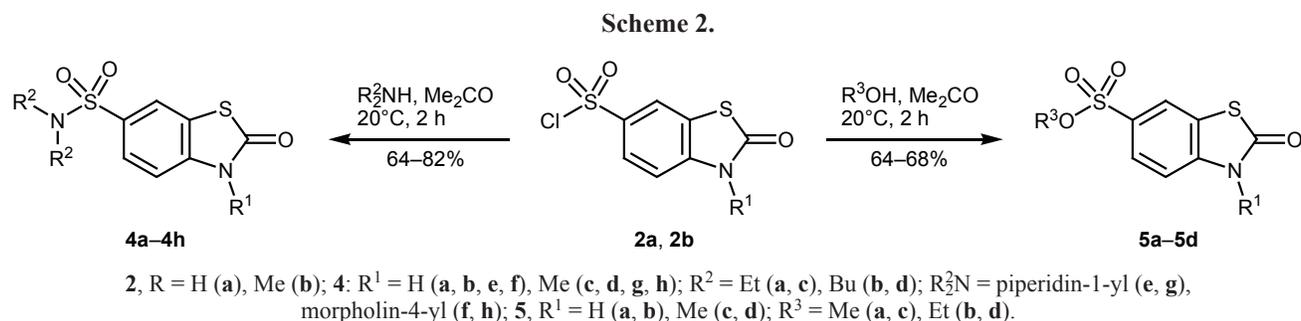
Benzothiazole derivatives have attracted much interest due to their high biological activity and broad spectrum of action [2–5]. In particular, compounds exhibiting fungicidal [2], herbicidal [3], growth-stimulating [4], and defoliating activities [5] were found among benzothiazole derivatives. In continuation of our studies on electrophilic substitution in the series of nitrogen heterocycles [6–11], herein we report chlorosulfonation of 1,3-benzothiazol-2(3H)-one (**1a**) and 3-methyl-1,3-benzothiazol-2(3H)-one (**1b**) and some chemical transformations of their chlorosulfonyl derivatives.

Compounds **1a** and **1b** reacted with chlorosulfonic acid to give the corresponding 6-chlorosulfonyl derivatives **2a** and **2b**, regardless of the reactant ratio. The best yields of **2a** and **2b** (83 and 87%, respectively) were obtained using 5 equiv of chlorosulfonic acid (Scheme 1). It should be noted that intermediate 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonic acids **3a** and **3b** could not be isolated. Presumably, the hydroxy group on the sulfur atom is readily replaced by chlorine due to increased positive charge on the sulfonyl sulfur atom. Sulfonic acids **3a** and **3b** were obtained with high yields by hydrolysis of **2a** and **2b**, respectively. In

Scheme 1.



¹ For communication II, see [1].



turn, sulfonic acids **3a** and **3b** were smoothly and quantitatively converted to sulfonyl chlorides **2a** and **2b** by treatment with chlorosulfonic acid (Scheme 1).

Sulfonyl chlorides **2a** and **2b** readily reacted with aliphatic (diethylamine, dibutylamine) and heterocyclic secondary amines (piperidine, morpholine) at room temperature in acetone in the presence of triethylamine to produce the corresponding *N,N*-dialkyl sulfonamides **4a–4h** with high yields. Sulfonic acid esters **5a–5d** were synthesized by reacting **2a** and **2b** with methanol and ethanol (Scheme 2).

The structure of compounds **2–5** was confirmed by IR, ¹H NMR, and mass spectra and elemental analyses. The IR spectra of **2–5** characteristically showed asymmetric (1220–1409 cm⁻¹) and symmetric (1055–1215 cm⁻¹) stretching vibration bands of the sulfonyl group, as well as C–S stretchings at 709–756 cm⁻¹. In addition, the IR spectra of **3a** and **3b** contained an absorption band at 645–655 cm⁻¹ due to S–O stretching vibrations. Out-of-plane C–H bending vibrations of the 1,2,4-trisubstituted benzene ring were observed at 805–825 and 870–880 cm⁻¹.

The mass spectra of **2–5** displayed the molecular and fragment ion peaks in agreement with the proposed structures. Fragmentation of the molecular ion of **2a** involves initial dissociation of the S–Cl bond with the

formation of fragment ion with *m/z* 214. Methyl-substituted analog **2b** decomposed via elimination of methyl radical with the formation of fragment ion with *m/z* 248 (Fig. 1). Regardless of the substituent on the benzothiazole nitrogen atom and on C⁶, the mass spectra of sulfonamides **4** and sulfonic acid esters **5** showed similar fragmentation patterns involving cleavage of the SO₂–N or SO₂–O bond and formation of fragments **A** and **B** (Fig. 2).

The ¹H NMR spectra of **2–5** contained signals from aromatic protons at δ 7.02–7.21 (d, *J*_{4,5} = 8.4–8.9 Hz, 4-H), 7.59–7.79 (d.d, *J*_{5,4} = 8.4–8.9 Hz, *J*_{5,7} = 1.6–1.9 Hz, 5-H), and 7.76–7.95 ppm (d, *J*_{7,5} = 1.6–1.9 Hz, 7-H). The N³H proton resonated at a low field (δ 9.17–9.31 ppm), and signals of alkyl protons in the amide or ester moiety were located in the expected upfield regions (δ 0.77–3.73 ppm).

EXPERIMENTAL

The IR spectra were recorded in KBr on a Perkin Elmer 2000 spectrometer (USA). The ¹H NMR spectra were run on a Varian Unity 400 Plus spectrometer (USA) at 400 MHz using DMSO-*d*₆ as solvent and tetramethylsilane as internal standard. The mass spectra (electron impact, 70 eV) were obtained on a Kratos MS-30 mass spectrometer (UK) with direct sample

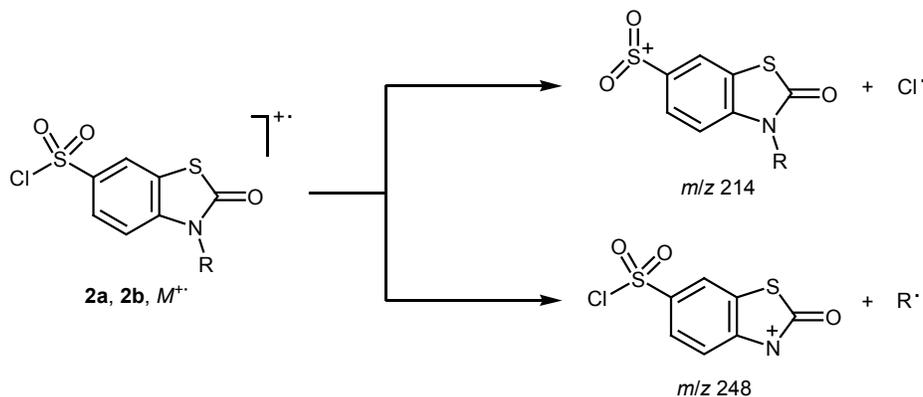


Fig. 1. Fragmentation of sulfonyl chlorides **2a** and **2b** under electron impact.

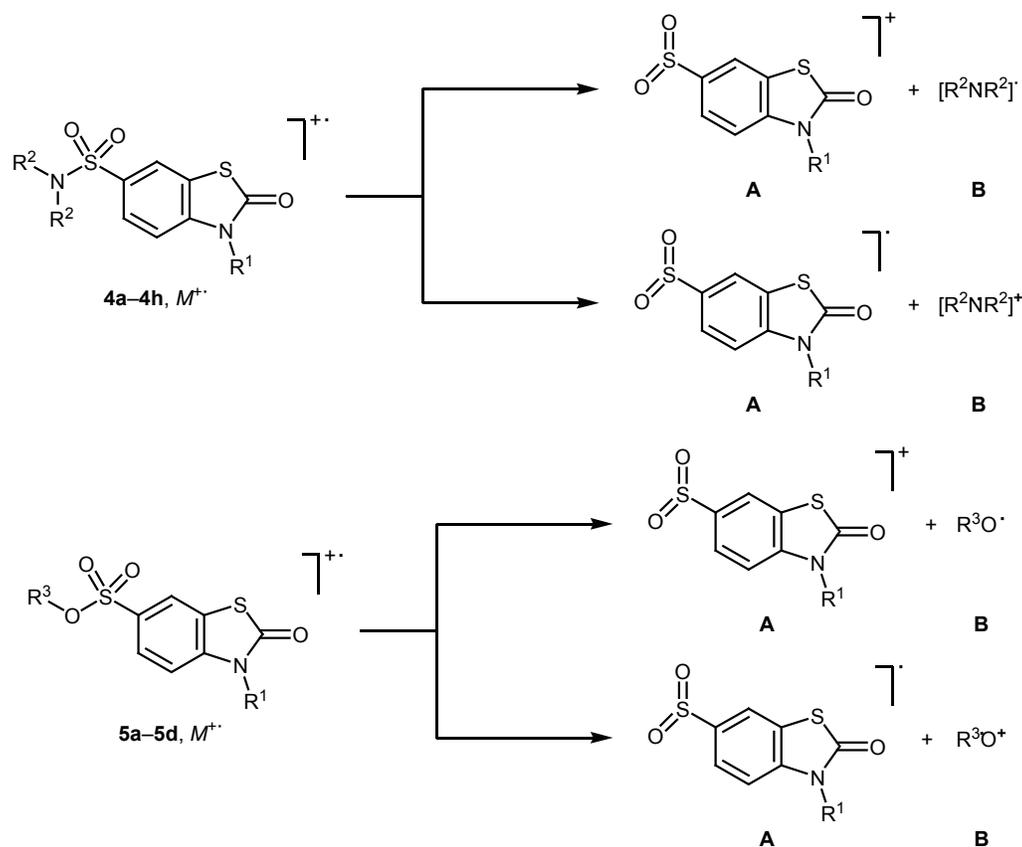


Fig. 2. Fragmentation of sulfonamides **4a–4h** and sulfonic acid esters **5a–5d** under electron impact.

admission into the ion source. The elemental analyses were carried out with a EuroVector EA-3000 automated CHNS analyzer (Italy). The melting points were measured on Boetius (Germany) and MEL-TEMP (USA) melting point apparatuses. The progress of reactions and the purity of the isolated compounds were monitored by TLC on Silufol UV-254 plates using benzene–acetone (10:1) as eluent; spots were visualized under UV light and by treatment with iodine vapor.

Initial 1,3-benzothiazol-2(3*H*)-one (**1a**) was synthesized by oxidation of 1,3-benzothiazole-2(3*H*)-thione with potassium permanganate, and 3-methyl-1,3-benzothiazol-2(3*H*)-one (**1b**) was prepared by phase-transfer alkylation of **1a** with dimethyl sulfate.

Sulfonyl chlorides **2a** and **2b** (general procedures).

a. Chlorosulfonic acid, 5.83 g (50 mmol), was cooled to 5–10°C, and 10 mmol of compound **1a** or **1b** was added in portions with stirring at such a rate that the temperature did not exceed 15°C. The mixture was then heated to 50–60°C, kept for 2 h at that temperature, and poured onto crushed ice. The precipitate of **2a** or **2b** was filtered off, washed with water, and recrystallized.

2-Oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonyl chloride (2a). Yield 2.07 g (83%), colorless crystals, mp 168–170°C (from heptane). IR spectrum, ν , cm^{-1} : 1365 s (SO_2 , asym.), 1175 s (SO_2 , sym.), 725 s (C–S). ^1H NMR spectrum, δ , ppm: 7.14 d (1H, 4-H, $J = 8.4$ Hz), 7.79 d.d (1H, 5-H, $J = 1.6, 8.4$ Hz), 7.95 d (1H, 7-H, $J = 1.6$ Hz), 9.31 s (1H, NH). Mass spectrum: m/z 249 (I_{rel} 81%) (^{35}Cl). Found, %: C 33.43; H 1.58; N 5.83; S 25.52. $\text{C}_7\text{H}_4\text{ClNO}_3\text{S}_2$. Calculated, %: C 33.66; H 1.60; N 5.61; S 25.65.

3-Methyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonyl chloride (2b). Yield 2.29 g (87%), colorless crystals, mp 151–152°C (from benzene). IR spectrum, ν , cm^{-1} : 1370 s (SO_2 , asym.), 1181 s (SO_2 , sym.), 730 s (C–S). ^1H NMR spectrum, δ , ppm: 3.41 s (3H, CH_3), 7.21 d (1H, 4-H, $J = 8.4$ Hz), 7.77 d.d (1H, 5-H, $J = 1.6, 8.4$ Hz), 7.93 d (1H, 7-H, $J = 1.6$ Hz). Mass spectrum: m/z 263 (I_{rel} 81%) [M] $^+$ (^{35}Cl). Found, %: C 36.27; H 2.19; N 5.12; S 24.14. $\text{C}_8\text{H}_6\text{ClNO}_3\text{S}_2$. Calculated, %: C 36.43; H 2.27; N 5.31; S 24.29.

b. Chlorosulfonic acid, 2.33 g (20 mmol), was cooled to 0°C, and 10 mmol of sulfonic acid **3a** or **3b** was added in portions with stirring at such a rate that

the temperature did not exceed 10°C. The mixture was then heated to 50–60°C, kept at that temperature for 1 h, and poured onto crushed ice. The precipitate was filtered off, washed with water, and recrystallized. Yield 96% (**2a**), 98% (**2b**). The products were identical to samples prepared as described above in *a* (no depression of the melting point was observed on mixing).

Sulfonic acids 3a and 3b (general procedure).

A mixture of 10 mmol of compound **2a** or **2b** and 20 mL of water was refluxed for 2 h. The mixture was partially evaporated, and the precipitate was filtered off and recrystallized from water.

2-Oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonic acid (3a). Yield 2.10 g (91%), colorless crystals, mp 238–240°C (from H₂O). IR spectrum, ν , cm⁻¹: 1220 s (SO₂, asym.), 1055 s (SO₂, sym.), 745 s (C–S), 645 s (S–O). ¹H NMR spectrum, δ , ppm: 7.04 d (1H, 4-H, *J* = 8.5 Hz), 7.68 d.d (1H, 5-H, *J* = 1.6, 8.5 Hz), 7.82 d (1H, 7-H, *J* = 1.6 Hz), 9.27 s (1H, NH). Mass spectrum: *m/z* 231 (*I*_{rel} 38%) [*M*]⁺. Found, %: C 36.15; H 2.11; N 5.83; S 27.58. C₇H₅NO₄S₂. Calculated, %: C 36.36; H 2.16; N 6.06; S 27.70.

3-Methyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonic acid (3b). Yield 2.25 g (92%), colorless crystals, mp 228–230°C (from H₂O). IR spectrum, ν , cm⁻¹: 1230 s (SO₂, asym.), 1070 s (SO₂, sym.), 757 s (C–S), 655 s (S–O). ¹H NMR spectrum, δ , ppm: 3.40 s (3H, CH₃), 7.09 d (1H, 4-H, *J* = 8.6 Hz), 7.68 d.d (1H, 5-H, *J* = 1.7, 8.6 Hz), 7.83 d (1H, 7-H, *J* = 1.7 Hz). Mass spectrum: *m/z* 245 (*I*_{rel} 41%) [*M*]⁺. Found, %: C 39.06; H 2.78; N 5.82; S 25.88. C₈H₇NO₄S₂. Calculated, %: C 39.18; H 2.86; N 6.06; S 26.12.

Sulfonamides 4a–4h (general procedure). Compound **2a** or **2b**, 10 mmol, was dissolved in 20 mL of acetone, and a solution of 10 mmol of the corresponding secondary amine and 1.01 g (10 mmol) of triethylamine in 10 mL of acetone was added dropwise. The mixture was stirred at room temperature for 2 h, the solvent was distilled off, the residue was treated with 100 mL of water, and the precipitate was filtered off and purified by recrystallization.

***N,N*-Diethyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonamide (4a).** Yield 1.86 g (65%), colorless crystals, mp 150–152°C (from EtOH). IR spectrum, ν , cm⁻¹: 1347 s (SO₂, asym.), 1175 s (SO₂, sym.), 746 s (C–S). ¹H NMR spectrum, δ , ppm: 1.05 t (6H, CH₂CH₃, *J* = 7.2 Hz), 2.47 q (4H, NCH₂, *J* = 7.2 Hz), 7.09 d (1H, 4-H, *J* = 8.9 Hz), 7.75 d.d (1H, 5-H, *J* = 1.8, 8.9 Hz), 7.92 d (1H, 7-H, *J* = 1.8 Hz), 9.21 s (1H, NH). Mass spectrum: *m/z* 286 (*I*_{rel} 29%) [*M*]⁺.

Found, %: C 45.87; H 4.78; N 10.01; S 22.22. C₁₁H₁₄N₂O₃S₂. Calculated, %: C 46.15; H 4.89; N 9.79; S 22.37.

***N,N*-Dibutyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonamide (4b).** Yield 2.29 g (67%), colorless crystals, mp 95–97°C (from EtOH). IR spectrum, ν , cm⁻¹: 1354 s (SO₂, asym.), 1164 s (SO₂, sym.), 734 s (C–S). ¹H NMR spectrum, δ , ppm: 0.83–0.91 m (6H, CH₃), 1.12–1.16 m (4H, CH₂CH₃), 1.38–1.46 m (4H, NCH₂CH₂), 3.11–3.21 m (4H, NCH₂), 7.14 d (1H, 4-H, *J* = 8.9 Hz), 7.73 d.d (1H, 5-H, *J* = 1.8, 8.9 Hz), 7.89 d (1H, 7-H, *J* = 1.8 Hz), 9.19 s (1H, NH). Mass spectrum: *m/z* 342 (*I*_{rel} 32%) [*M*]⁺. Found, %: C 52.37; H 6.29; N 7.99; S 18.52. C₁₅H₂₂N₂O₃S₂. Calculated, %: C 52.63; H 6.43; N 8.18; S 18.71.

***N,N*-Diethyl-3-methyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonamide (4c).** Yield 2.46 g (82%), colorless crystals, mp 136–138°C (from EtOH–H₂O). IR spectrum, ν , cm⁻¹: 1353 s (SO₂, asym.), 1167 s (SO₂, sym.), 756 s (C–S). ¹H NMR spectrum, δ , ppm: 1.08 t (6H, CH₂CH₃, *J* = 7.2 Hz), 2.53 q (4H, NCH₂, *J* = 7.2 Hz), 7.02 d (1H, 4-H, *J* = 8.6 Hz), 7.69 d.d (1H, 5-H, *J* = 1.8, 8.6 Hz), 7.85 d (1H, 7-H, *J* = 1.8 Hz). Mass spectrum: *m/z* 300 (*I*_{rel} 36%) [*M*]⁺. Found, %: C 47.72; H 5.15; N 9.61; S 21.21. C₁₂H₁₆N₂O₃S₂. Calculated, %: C 47.99; H 5.33; N 9.33; S 21.33.

***N,N*-Dibutyl-3-methyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonamide (4d).** Yield 2.35 g (66%), colorless crystals, mp 91–92°C (from EtOH–H₂O). IR spectrum, ν , cm⁻¹: 1348 s (SO₂, asym.), 1164 s (SO₂, sym.), 741 s (C–S). ¹H NMR spectrum, δ , ppm: 0.77–0.87 m (6H, CH₂CH₃), 1.38–1.46 m (4H, CH₂CH₃), 1.57–1.64 m (4H, NCH₂CH₂), 3.11–3.21 m (4H, NCH₂), 3.39 s (3H, 3-CH₃), 7.05 d (1H, 4-H, *J* = 8.7 Hz), 7.69 d.d (1H, 5-H, *J* = 1.7, 8.7 Hz), 7.87 d (1H, 7-H, *J* = 1.7 Hz). Mass spectrum: *m/z* 356 (*I*_{rel} 28%) [*M*]⁺. Found, %: C 53.77; H 6.66; N 8.15; S 17.76. C₁₆H₂₄N₂O₃S₂. Calculated, %: C 53.93; H 6.74; N 7.86; S 17.97.

6-(Piperidin-1-ylsulfonyl)-1,3-benzothiazol-2(3*H*)-one (4e). Yield 2.11 g (71%), colorless crystals, mp 211–213°C (from EtOH). IR spectrum, ν , cm⁻¹: 1343 s (SO₂, asym.), 1166 s (SO₂, sym.), 745 s (C–S). ¹H NMR spectrum, δ , ppm: 2.44–2.49 m (2H, 4'-H), 2.86 q (4H, 3'-H, 5'-H, *J* = 6.9 Hz), 3.61 q (4H, 2'-H, 6'-H, *J* = 6.9 Hz), 7.04 d (1H, 4-H, *J* = 8.9 Hz), 7.65 d.d (1H, 5-H, *J* = 1.8, 8.9 Hz), 7.79 d (1H, 7-H, *J* = 1.8 Hz), 9.18 s (1H, NH). Mass spectrum: *m/z* 298 (*I*_{rel} 100%) [*M*]⁺. Found, %: C 48.09; H 4.57; N 9.09; S 21.22. C₁₂H₁₄N₂O₃S₂. Calculated, %: C 48.32; H 4.69; N 9.39; S 21.47.

6-(Morpholin-4-ylsulfonyl)-1,3-benzothiazol-2(3H)-one (4f). Yield 2.07 g (69%), colorless crystals, mp 213–215°C (from EtOH). IR spectrum, ν , cm^{-1} : 1345 s (SO_2 , asym.), 1169 s (SO_2 , sym.), 749 s (C–S). ^1H NMR spectrum, δ , ppm: 2.87 t (4H, CH_2OCH_2 , $J = 7.9$ Hz), 3.60 t (4H, CH_2NCH_2 , $J = 7.9$ Hz), 7.07 d (1H, 4-H, $J = 8.8$ Hz), 7.68 d.d (1H, 5-H, $J = 1.8$, 8.8 Hz), 7.81 d (1H, 7-H, $J = 1.8$ Hz), 9.17 s (1H, NH). Mass spectrum: m/z 300 (I_{rel} 56%) [M] $^+$. Found, %: C 43.87; H 3.87; N 9.61; S 21.14. $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$. Calculated, %: C 44.00; H 3.99; N 9.33; S 21.33.

3-Methyl-6-(piperidin-1-ylsulfonyl)-1,3-benzothiazol-2(3H)-one (4g). Yield 2.09 g (67%), colorless crystals, mp 201–203°C (from EtOH– H_2O). IR spectrum, ν , cm^{-1} : 1346 s (SO_2 , asym.), 1166 s (SO_2 , sym.), 747 s (C–S). ^1H NMR spectrum, δ , ppm: 2.46–2.51 m (2H, 4'-H), 2.85 t (4H, 3'-H, 5'-H, $J = 6.9$ Hz), 3.39 s (3H, 3- CH_3), 3.61 t (4H, 2'-H, 6'-H, $J = 6.9$ Hz), 7.06 d (1H, 4-H, $J = 8.9$ Hz), 7.71 d.d (1H, 5-H, $J = 1.7$, 8.6 Hz), 7.79 d (1H, 7-H, $J = 1.7$ Hz). Mass spectrum: m/z 312 (I_{rel} 100%) [M] $^+$. Found, %: C 49.81; H 5.02; N 9.15; S 20.28. $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3\text{S}_2$. Calculated, %: C 50.02; H 5.13; N 8.97; S 20.51.

3-Methyl-6-(morpholin-4-ylsulfonyl)-1,3-benzothiazol-2(3H)-one (4h). Yield 2.01 g (64%), colorless crystals, mp 227–229°C (from EtOH– H_2O). IR spectrum, ν , cm^{-1} : 1353 s (SO_2 , sym.), 1152 s (SO_2 , sym.), 753 s (C–S). ^1H NMR spectrum, δ , ppm: 2.86 t (4H, CH_2OCH_2 , $J = 8.0$ Hz), 3.39 s (3H, 3- CH_3), 3.59 t (4H, CH_2NCH_2 , $J = 8.0$ Hz), 7.04 d (1H, 4-H, $J = 8.6$ Hz), 7.65 d.d (1H, 5-H, $J = 1.8$, 8.6 Hz), 7.76 d (1H, 7-H, $J = 1.8$ Hz). Mass spectrum: m/z 314 (I_{rel} 47%) [M] $^+$. Found, %: C 45.57; H 4.33; N 8.65; S 20.12. $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_4\text{S}_2$. Calculated, %: C 45.85; H 4.45; N 8.91; S 20.38.

Sulfonic acid esters 5a–5d (general procedure). A solution of 10 mmol of methanol or ethanol and 1.01 g (10 mmol) of triethylamine in 10 mL of acetone was added dropwise to a solution of 10 mmol of compound **2** in 20 mL of acetone. The mixture was stirred at room temperature for 2 h, the solvent was distilled off, and the residue was treated with 100 mL of water. The precipitate of **5a–5d** was filtered off and purified by recrystallization.

Methyl 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonate (5a). Yield 1.64 g (67%), colorless crystals, mp 165–167°C (from EtOH). IR spectrum, ν , cm^{-1} : 1417 s (SO_2 , asym.), 1205 s (SO_2 , sym.), 709 s (C–S). ^1H NMR spectrum, δ , ppm: 3.73 s (3H, OCH_3), 7.05 d (1H, 4-H, $J = 8.7$ Hz), 7.66 d.d (1H, 5-H, $J = 1.7$, 8.7 Hz), 7.79 d (1H, 7-H, $J = 1.7$ Hz), 9.18 s (1H, NH).

Mass spectrum: m/z 245 (I_{rel} 39%) [M] $^+$. Found, %: C 38.92; H 2.71; N 5.92; S 25.88. $\text{C}_8\text{H}_7\text{NO}_4\text{S}_2$. Calculated, %: C 39.18; H 2.85; N 5.71; S 26.12.

Ethyl 2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonate (5b). Yield 1.76 g (68%), colorless crystals, mp 156–158°C (from EtOH). IR spectrum, ν , cm^{-1} : 1409 s (SO_2 , asym.), 1196 s (SO_2 , sym.), 714 s (C–S). ^1H NMR spectrum, δ , ppm: 3.68 t (3H, CH_2CH_3 , $J = 7.1$ Hz), 4.06 q (2H, OCH_2 , $J = 7.1$ Hz), 7.03 d (1H, 4-H, $J = 8.8$ Hz), 7.64 d.d (1H, 5-H, $J = 1.9$, 8.8 Hz), 7.76 d (1H, 7-H, $J = 1.9$ Hz), 9.19 s (1H, NH). Mass spectrum: m/z 259 (I_{rel} 51%) [M] $^+$. Found, %: C 41.42; H 3.39; N 5.26; S 24.49. $\text{C}_9\text{H}_9\text{NO}_4\text{S}_2$. Calculated, %: C 41.69; H 3.47; N 5.40; S 24.71.

Methyl 3-methyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonate (5c). Yield 1.65 g (64%), colorless crystals, mp 142–144°C (from EtOH– H_2O). IR spectrum, ν , cm^{-1} : 1402 s (SO_2 , asym.), 1215 s (SO_2 , asym.), 718 s (C–S). ^1H NMR spectrum, δ , ppm: 3.46 s (3H, 3- CH_3), 3.71 s (3H, OCH_3), 7.09 d (1H, 4-H, $J = 8.7$ Hz), 7.59 d.d (1H, 5-H, $J = 1.7$, 8.7 Hz), 7.76 d (1H, 7-H, $J = 1.7$ Hz). Mass spectrum: m/z 259 (I_{rel} 29%) [M] $^+$. Found, %: C 41.39; H 3.35; N 5.56; S 24.38. $\text{C}_9\text{H}_9\text{NO}_4\text{S}_2$. Calculated, %: C 41.69; H 3.47; N 5.40; S 24.71.

Ethyl 3-methyl-2-oxo-2,3-dihydro-1,3-benzothiazole-6-sulfonate (5d). Yield 1.80 g (66%), colorless crystals, mp 129–131°C (from EtOH– H_2O). IR spectrum, ν , cm^{-1} : 1405 s (SO_2 , asym.), 1207 s (SO_2 , sym.), 716 s (C–S). ^1H NMR spectrum, δ , ppm: 3.45 s (3H, 3- CH_3), 3.70 t (3H, CH_2CH_3 , $J = 7.1$ Hz), 4.08 q (2H, OCH_2 , $J = 7.1$), 7.08 d (1H, 4-H, $J = 8.9$ Hz), 7.62 d.d (1H, 5-H, $J = 1.8$, 8.9 Hz), 7.81 d (1H, 7-H, $J = 1.8$ Hz). Mass spectrum: m/z 273 (I_{rel} 32%) [M] $^+$. Found, %: C 43.77; H 3.94; N 4.88; S 23.25. $\text{C}_{10}\text{H}_{11}\text{NO}_4\text{S}_2$. Calculated, %: C 43.95; H 4.03; N 5.12; S 23.44.

CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

REFERENCES

1. Kaipnazarov, T.N., Mukhamedov, N.S., Okmanov, R.Y., Berdimbetova, G.E., and Zhonkhozhayeva, F.B., *Russ. J. Org. Chem.*, 2013, vol. 49, p. 1744. <https://doi.org/10.1134/S1070428013120063>
2. Graham, H.P. and Pomfret, V.J., UK Patent no. 137975, 1974; *Ref. Zh., Khim.*, 1975, no. 23O407.
3. Baskakov, Yu.A., *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva*, 1984, vol. 29, p. 22.

4. Damico, J.J. and Morvell, J.T., US Patent no. 4283220, 1981; *Ref. Zh., Khim.*, 1982, no. 8O410.
5. Rozhkova, N.K., Abstracts of Papers, *Materialy I Vsesoyuznogo soveshchaniya po defoliatsii i desikatsii sel'skokhozyaistvennykh kul'tur* (Proc. Ist All-Union Meet. on Defoliation and Desiccation of Crops), Tashkent, 1974, p. 35.
6. Dushamov, D.A., Mukhamedov, N.S., Bobokulov, Kh.M., and Aliev, N.A., *Khim. Prir. Soedin.*, 2001, vol. 10, special issue, p. 83.
7. Mukhamedov, N.S., Dushamov, D.A., Aliyev, N.A., Bobokulov, Kh.M., Levkovich, M.G., and Abdullaev, N.D., *Chem. Heterocycl. Compd.*, 2002, vol. 38, p. 344.
<https://doi.org/10.1023/A:1015647606680>
8. Mukhamedov, N.S., Dushamov, D.A., Aliyev, N.A., Bobokulov, Kh.M., Levkovich, M.G., and Abdullaev, N.D., *Chem. Heterocycl. Compd.*, 2002, vol. 38, p. 438.
<https://doi.org/10.1023/A:1016083322553>
9. Zhumaniyazova, M.E., Yakubov, U.Kh., Dushamov, D.A., Mukhamedov, N.S., Zhonkhozhaev, F.B., and Aliev, N.A., *Uzb. Khim. Zh.*, 2004, no. 3, p. 34.
10. Takhirov, Yu.R., Dushamov, D.A., Mukhamedov, N.S., and Shakhidoyatov, Kh.M., *Khim. Khim. Tekhnol.*, 2010, no. 1, p. 18.
11. Karimova, M.E., Dushamov, D.A., Kuryazov, R.Sh., and Mukhamedov, N.S., *Chem. Heterocycl. Compd.*, 2011, vol. 47, p. 90.
<https://doi.org/10.1007/s10593-01-0724-1>