ISSN 1070-4280, Russian Journal of Organic Chemistry, 2020, Vol. 56, No. 3, pp. 458–464. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Zhurnal Organicheskoi Khimii, 2020, Vol. 56, No. 3, pp. 456–463.

Synthesis of the 1-Bromotricyclo[4.1.0.0^{2,7}]heptane Adduct with 2-Bromoethanesulfonyl Bromide and Its Transformations

S. G. Kostryukov[a,*] and Yu. Yu. Masterova[a]

[a] *Ogarev Mordovian National Research State University, Saransk, 430005 Russia*

**e-mail: kostryukov_sg@mail.ru*

Received November 21, 2019; revised January 18, 2020; accepted January 20, 2020

Abstract—The addition of 2-bromoethanesulfonyl bromide to 1-bromotricyclo[4.1.0.0^{2,7}]heptane at the C^1–C^7 central bicyclobutane bond follows a radical mechanism to give 1:1 adduct with a bicyclo[3.1.1]heptane structure. Treatment of the adduct with triethylamine leads to the formation of vinyl sulfone as a result of 1,2-dehydrobromination, and its reaction with 2 equiv of sodium methoxide involves 1,2- and 1,3-dehydrobromination to afford 7-bromo-1-(ethenesulfonyl)tricyclo[4.1.0.0^{2,7}]heptane. The latter is capable of reacting with sodium methoxide and sodium methanesulfonate to form nucleophilic addition products.

Keywords: 2-bromoethanesulfonyl bromide, 1-bromotricyclo[4.1.0.0^{2,7}]heptane, radical addition, bicyclo[3.1.1]heptane, dehydrobromination, vinyl sulfone

DOI: 10.1134/S107042802003015X

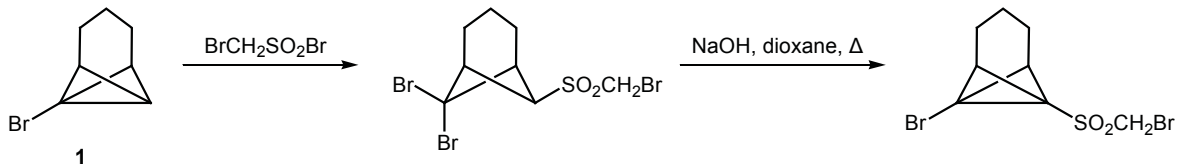
It is known [1–4] that bromomethanesulfonyl bromide reacts with alkenes to give α,β′-dibromo sulfones which undergo dehydrobromination and desulfonation by the action of bases with the formation of conjugated dienes. Bromomethanesulfonyl bromide reacts with 1-bromotricyclo[4.1.0.0^{2,7}]heptane (**1**) in a similar way [5] to produce a bicyclo[3.1.1]heptane (norpinane) derivative with *syn* orientation of the bromomethanesulfonyl group. Treatment of the adduct with sodium hydroxide in aqueous dioxane leads to the formation of 2-bromo-1-(bromomethanesulfonyl)tricyclo[4.1.0.0^{2,7}]heptane as a result of 1,3-dehydrobromination (Scheme 1).

Due to the presence of a bromine atom, 1-bromotricyclo[4.1.0.0^{2,7}]heptane (**1**) possesses a significant synthetic potential. For example, the adduct of **1** and hydrogen sulfide was converted to bis(tricyclo[4.1.0.0^{2,7}]heptan-1-yl) sulfoxide and the corresponding sulfone [6]. 6-Norpinanones and 6-norpinanethiones were obtained by alkaline treatment of the adducts of **1** with benzenesulfonyl bromide [7] and benzenesulfonyl and methanesulfonyl thiocyanates [8]. Therefore, reactions of 1-bromotricycloheptane **1** with other sulfonating agents are of great interest as they could give rise to new sulfones of the tricyclo- and bicycloheptane series.

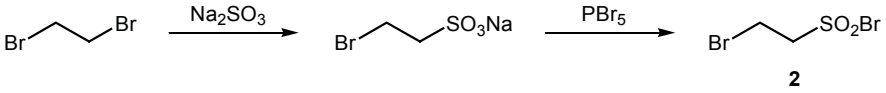
With the goal of extending the series of available haloalkanesulfonyl halides, in this work we have synthesized 2-bromoethanesulfonyl bromide (**2**) and studied its reaction with tricycloheptane **1**. We have found no published data on the synthesis of sulfonyl bromide **2**, and it was prepared according to the procedure proposed previously for the synthesis of iodomethanesulfonyl bromide [4]. For this purpose, by reacting excess 1,2-dibromoethane with sodium sulfite we obtained sodium 2-bromoethane-1-sulfonate [9], and the latter was treated with phosphorus(V) bromide (Scheme 2).

The reaction of 1-bromotricyclo[4.1.0.0^{2,7}]heptane (**1**) with sulfonyl bromide **2** was carried out by mixing the reactants at 0°C in anhydrous methylene chloride in

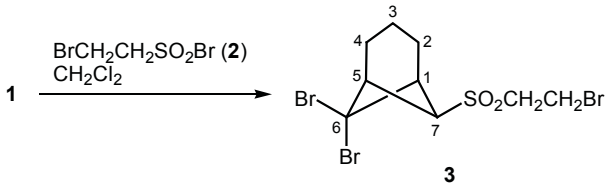
Scheme 1.



Scheme 2.



Scheme 3.



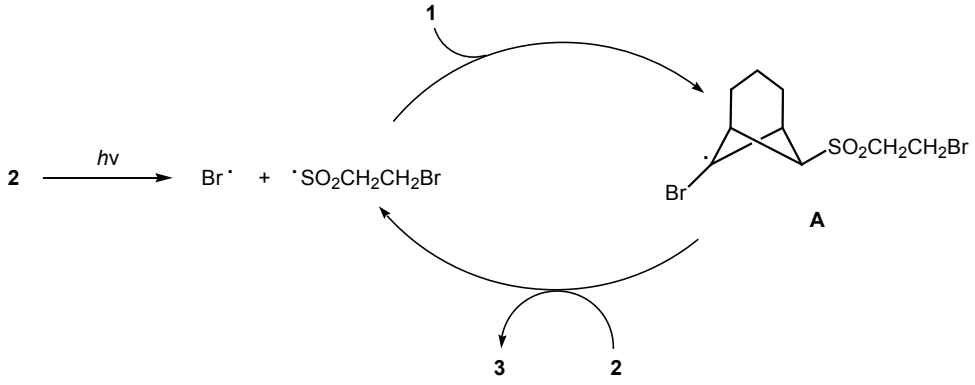
the presence of anhydrous sodium carbonate, followed by keeping the mixture at room temperature on exposure to scattered sunlight for 10 h; the consumption of **2** was monitored by TLC. The corresponding 1 : 1 adduct, 6,6-dibromo-7-(2-bromoethanesulfonyl)bicyclo[3.1.1]heptane (**3**) was isolated in a high yield (Scheme 3) by crystallization and was characterized by IR and ^{1}H and ^{13}C NMR spectra and elemental analysis.

The bicyclo[3.1.1]heptane structure of **3** was confirmed by the presence in its ^{13}C NMR spectrum of five signals for seven carbon atoms of the norpinane skeleton in expected positions and with expected intensities. The configuration of C^7 was assigned by analysis of the position and multiplicity of the 7-H signal in the ^{1}H NMR spectrum with account taken of known correlations [5–8, 10, 11]. In particular, the 7-H signal appeared as a triplet, which suggests its *anti* orientation with respect to the trimethylene bridge. The sulfonyl group characteristically gave rise to strong absorption bands in the IR spectrum at ~1130 and ~1330 cm^{-1} [12].

Thus, like bromomethanesulfonyl bromide [5], arenesulfonyl halides [7, 10, 11], and some other sulfonyl derivatives [8], 2-bromoethanesulfonyl bromide (**2**) adds to tricycloheptane **1** exclusively at the central C^1–C^7 bond. On the basis of our previous considerations [7, 8, 10, 11], these reactions should be assumed to follow a radical mechanism (Scheme 4). As in other cases [5], the reaction is initiated by the *endo* attack of sulfonyl radical on the sterically more accessible unsubstituted C^7 atom of 1-bromotricyclo[4.1.0.0^{2,7}]-heptane (**1**) with high regioselectivity. The subsequent bromine transfer to bicyclo[3.1.1]heptyl intermediate **A** involves predominantly the *exo* position, which however does not matter for the bromo-substituted substrate, since in any case the same product **3** is formed.

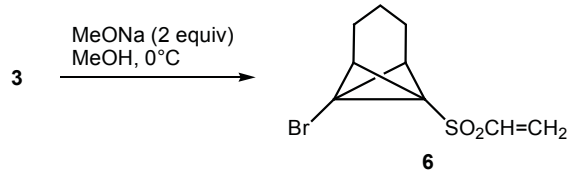
Due to the presence of a 2-bromoethanesulfonyl substituent, compound **3** can be subjected to various transformations by the action of nucleophiles and bases. The reaction of **3** with an equimolar amount of triethylamine in benzene gave vinyl sulfone **4** as a result of 1,2-dehydrobromination. The same product was formed in the reaction of **3** with an equimolar amount of sodium methoxide in methanol at 0°C, but in this case the reaction was accompanied by the formation of tricycloheptane **5** (Scheme 5). According to the ^{1}H NMR data, the ratio **4**/**5** was 65:35. When the reaction was carried out with 2 equiv of sodium

Scheme 4.



Scheme 5.

Scheme 6.



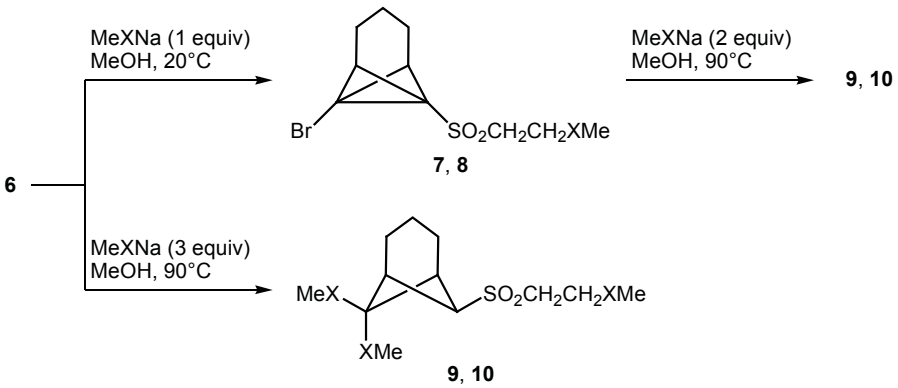
methoxide at 0°C, the only product was ethenesulfonyltricycloheptane **6** (Scheme 6).

Compound **6** is an interesting system containing a bicyclobutane moiety and C=C double bond, and it can be used as a model structure to study the relative reactivity of the bicyclobutane system and multiple bond toward nucleophiles. As shown previously [13], there is no linear correlation between the reactivities of bicyclobutane derivatives and analogous vinylic compounds. Olefinic systems containing an ester, sulfonyl, or cyano group proved to be more reactive than bicyclobutane derivatives with similar substituents [13].

We examined reactions of tricycloheptane **6** with sodium methoxide and sodium methanethiolate. An equimolar amount of the nucleophile was used with a view to determining whether the bicyclobutane or exocyclic C=C bond would be more reactive toward nucleophilic addition. The progress of reactions was monitored by TLC, and the product structure was determined on the basis of their ^{1}H and ^{13}C NMR spectra. Under the given conditions, both sodium methoxide and sodium methanethiolate added exclusively to the vinylsulfonyl fragment to give compounds **7** and **8** with the C^1–C^7 bond remaining intact (Scheme 7). The bicyclobutane moiety did not change in the reactions with 2 equiv of nucleophile. Only in the reaction with 3 equiv of MeONa or MeSNa under more severe conditions (heating at 90°C in a sealed ampule) we isolated products of addition to both C=C and C^1–C^7 bonds, bicycloheptanes **9** and **10**. Compounds **9** and **10** were also obtained from tricycloheptanes **7** and **8** under similar conditions (Scheme 7).

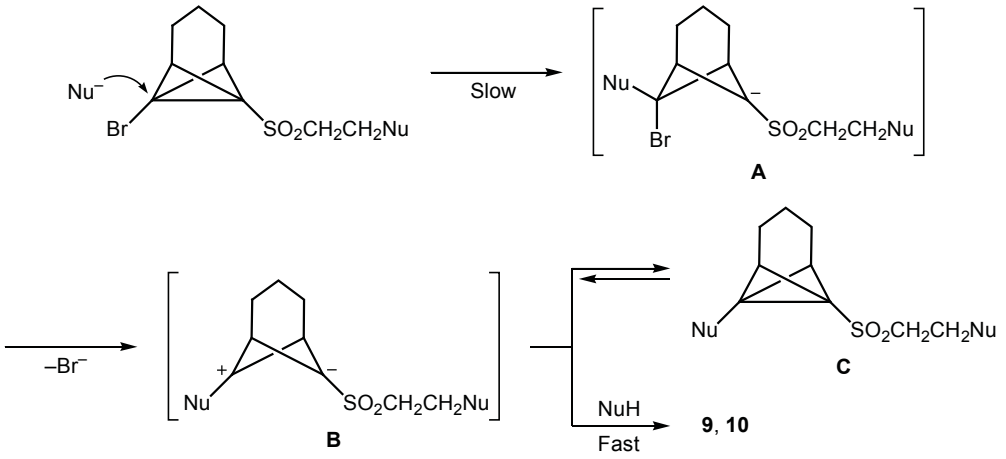
The formation of compounds **9** and **10** can be illustrated by Scheme 8. Initial nucleophilic attack on C^7 gives carbanion **A** which loses bromide ion to generate highly reactive zwitterionic intermediate **B**, and the latter is converted to bicycloheptane **9** and **10** via addition of the second nucleophile molecule. The formation of zwitterion **B** is indirectly supported by the fact that the reaction with 1 equiv of nucleophile would produce tricycloheptane **C**, whereas only compound **9** or **10** was detected in the reaction mixture.

Scheme 7.



7, **9**, X = O; **8**, **10**, X = S.

Scheme 8.



All sulfones **4**–**10** were isolated in the pure state and were characterized by ^{1}H and ^{13}C NMR and IR spectra, as well as elemental analyses.

Thus, 2-bromoethane-1-sulfonyl bromide is an efficient reagent for introducing a 2-bromoethanesulfonyl fragment. Its reaction with 1-bromotricyclo[4.1.0.0^{2,7}]-heptane gives only one product which can be converted to vinylsulfonyl-substituted bicycloheptane and tricycloheptane derivatives. 7-Bromo-1-(ethenesulfonyl)-tricyclo[4.1.0.0^{2,7}]heptane reacts with nucleophiles to give products of addition to both exocyclic C=C bond and bicyclobutane C^1–C^7 bond.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Jeol JNM-ECX400 spectrometer at 400 and 100 MHz, respectively, using the residual proton and carbon signals of the solvent as reference ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.16 ppm). The IR spectra were recorded on an InfraLYuM FT-02 spectrometer from samples prepared as KBr disks. Elemental analysis was carried out with a Vario MICRO CHNS analyzer. Analytical TLC was performed on Silufol UV-254 plates using light petroleum ether–diethyl ether (1:1) as eluent; spots were visualized by treatment with iodine vapor or under UV light. The products were isolated by dry-column flash chromatography on silica gel using hexane–diethyl ether (3:1 to 1:1) as eluent. The melting points were measured in sealed glass capillary tubes using an MP-50 melting point analyzer.

1-Bromotricyclo[4.1.0.0^{2,7}]heptane (**1**) [14] and sodium 2-bromoethane-1-sulfonate [9] were prepared according to reported procedures.

2-Bromoethane-1-sulfonyl bromide (2). A 500-mL round-bottom flask equipped with a reflux condenser was charged with 21.1 g (0.1 mol) of sodium 2-bromoethane-1-sulfonate, 51.7 g (0.12 mol) of phosphorus(V) bromide, and 150 mL of anhydrous methylene chloride. The mixture was refluxed for 6 h and cooled to 0°C, and ~250 g of crushed ice was added to the mixture. When the added ice melted, the organic phase was separated and dried over $CaCl_2$, the solvent was distilled under reduced pressure (10–20 mm Hg), and the residue was distilled in a vacuum (≤1 mm Hg) to collect a fraction boiling at 80–90°C. Repeated vacuum distillation gave 17 g (68%) of **2** with bp 88–89°C (0.5 mm Hg). IR spectrum, ν, cm^{-1}: 2950 w, 1364 s (SO_2, asym.), 1153 v.s (SO_2, sym.). ^{1}H NMR spectrum, δ, ppm: 3.75 t (2H, J = 8.0 Hz), 4.18 t (2H, J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.7 (C^2), 48.7 (C^1). Found, %: C 9.59; H 1.58. $C_2H_4Br_2O_2S$. Calculated, %: C 9.54; H 1.60.

Reaction of tricycloheptane 1 with 2-bromoethane-1-sulfonyl bromide (2). A mixture of 1.73 g (10 mmol) of tricycloheptane **1** in 15 mL of anhydrous methylene chloride and 0.5 g of anhydrous sodium carbonate was cooled to 0°C, and 2.52 g (10 mmol) of sulfonyl bromide **2** was added. The mixture was kept for 1 h at 0°C and for 10 h at room temperature, following the disappearance of **2** by TLC monitoring. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was analyzed by TLC and ^{1}H NMR and purified by recrystallization.

6,6-Dibromo-7-*syn*-(2-bromoethanesulfonyl)bicyclo[3.1.1]heptane (3). Yield 3.31 g (79%), mp 119–120°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2951 m, 1450 m, 1304 s (SO_2, asym.), 1288 s, 1134 v.s (SO_2, sym.), 1030 m, 740 s, 686 s. ^{1}H NMR spectrum,

δ, ppm: 0.86–0.99 m (1H, 3-*endo*-H), 1.03–1.14 m (1H, 3-*exo*-H), 1.43–1.55 m (2H, 2-*endo*-H, 4-*endo*-H), 1.58–1.70 m (2H, 2-*exo*-H, 4-*exo*-H), 2.57 br.d (2H, 1-H, 5-H), 2.72 t (2H, CH_2Br, J = 7.5 Hz), 2.88 t (2H, CH_2SO_2, J = 7.5 Hz), 3.56 t (1H, 7-*anti*-H, J = 5.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.8 (C^3), 20.7 (CH_2Br), 25.8 (C^2, C^4), 57.1 (C^6), 57.3 (C^1, C^5), 57.6 (CH_2SO_2), 65.8 (C^7). Found, %: C 25.46; H 3.10. $C_9H_{13}Br_3O_2S$. Calculated, %: C 25.44; H 3.08.

Reaction of bicycloheptane (3) with triethylamine. A solution of 0.069 mL (0.5 mmol) of triethylamine in 2.0 mL of anhydrous benzene was added to a solution of 212 mg (0.5 mmol) of compound **3** in 5 mL of anhydrous benzene. The mixture was stirred for 1 h at 0°C, and the precipitate of triethylamine hydrobromide was filtered off and washed with 10 mL of benzene. The filtrate was combined with the washings, washed with water (2×5 mL), and dried over $MgSO_4$. The solvent was distilled off on a rotary evaporator, and the crystalline residue was analyzed by ^1H and ^{13}C NMR and purified by recrystallization.

6,6-Dibromo-7-*syn*-(ethenesulfonyl)bicyclo[3.1.1]heptane (4). Yield 139 mg (81%), mp 94–95°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3092 m, 2951 m, 1648 m (C=C), 1448 m, 1310 s (SO_2, asym.), 1295 s, 1139 v.s (SO_2, sym.), 1031 m, 745 s, 690 s. ^1H NMR spectrum, δ, ppm: 0.91–1.02 m (1H, 3-*endo*-H), 1.10–1.20 m (1H, 3-*exo*-H), 1.55–1.67 m (2H, 2-*endo*-H, 4-*endo*-H), 1.76–1.88 m (2H, 2-*exo*-H, 4-*exo*-H), 2.91 br.d (2H, 1-H, 5-H), 3.59 t (1H, 7-*anti*-H, J = 5.6 Hz), 6.19 d.d (1H, CH_2=, J = 10.5, 1.7 Hz), 6.51 d.d (1H, CH_2=, J = 17.1, 1.7 Hz), 6.78 d.d (1H, SO_2CH=, J = 17.1, 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.5 (C^3), 23.5 (C^2, C^4), 47.8 (C^1, C^5), 58.3 (C^7), 57.5 (C^6), 130.5 (CH_2=), 137.2 (=$CHSO_2$). Found, %: C 31.41; H 3.50. $C_9H_{12}Br_2O_2S$. Calculated, %: C 31.42; H 3.52.

Reaction of bicycloheptane 3 with an equimolar amount of sodium methoxide. Compound **3**, 212 mg (0.5 mmol), was dissolved in 10 mL of anhydrous methanol, 1 mL of a 0.5 M solution of sodium methoxide was added, and the mixture was stirred for 1 h at 0°C. The solvent was removed under reduced pressure, the residue was dissolved in 15 mL of methylene chloride, and the solution was washed with water (2×5 mL) and dried over $MgSO_4$. The solvent was distilled off on a rotary evaporator, and the residue was analyzed by ^1H and ^{13}C NMR. The products were isolated by flash chromatography on silica gel.

6,6-Dibromo-7-*syn*-(ethenesulfonyl)bicyclo[3.1.1]heptane (4). Yield 78 mg (45%).

7-Bromo-1-(2-bromoethanesulfonyl)tricyclo[4.1.0.0^{2,7}]heptane (5). Yield 36 mg (21%), mp 59–60°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3040 w, 2945 m, 1485 m, 1450 m, 1331 s (SO_2, asym.), 1210 m, 1140 v.s (SO_2, sym.), 1120 m, 755 s, 661 m. ^1H NMR spectrum, δ, ppm: 1.21–1.48 m (2H, 4-H), 1.50–1.64 m (4H, 3-H, 5-H), 3.29 br.s (2H, 2-H, 6-H), 3.12 t (2H, CH_2Br, J = 7.5 Hz), 3.34 t (2H, CH_2SO_2, J = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.6 (C^3, C^5), 23.7 (CH_2Br), 24.2 (C^4), 31.9 (C^7), 35.6 (C^1), 49.1 (C^2, C^6), 57.6 (CH_2SO_2). Found, %: C 31.41; H 3.50. $C_9H_{12}Br_2O_2S$. Calculated, %: C 31.42; H 3.52.

Reaction of bicycloheptane 3 with 2 equiv of sodium methoxide. Compound **3**, 212 mg (0.5 mmol), was dissolved in 10 mL of anhydrous methanol, 2 mL of a 0.5 M solution of sodium methoxide in methanol was added, and the mixture was stirred for 1 h at 0°C. The solvent was removed under reduced pressure, the residue was dissolved in 15 mL of methylene chloride, and the solution was washed with water (2×5 mL) and dried over $MgSO_4$. The solvent was distilled off on a rotary evaporator, and the crystalline residue was analyzed by ^1H and ^{13}C NMR and purified by recrystallization.

7-Bromo-1-(ethenesulfonyl)tricyclo[4.1.0.0^{2,7}]heptane (6). Yield 85 mg (65%), mp 47–48°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3090 w, 2944 m, 1642 m (C=C), 1484 m, 1445 m, 1335 s (SO_2, asym.), 1208 m, 1142 v.s (SO_2, sym.), 1118 m, 750 s, 663 m. ^1H NMR spectrum, δ, ppm: 1.18–1.39 m (2H, 4-H), 1.45–1.60 m (4H, 3-H, 5-H), 3.21 br.s (2H, 2-H, 6-H), 6.11 d.d (1H, CH_2=, J = 10.5, 1.7 Hz), 6.46 d.d (1H, CH_2=, J = 17.1, 1.7 Hz), 6.65 d.d (1H, SO_2CH=, J = 17.1, 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.1 (C^3, C^5), 24.2 (C^4), 31.5 (C^7), 35.8 (C^1), 49.0 (C^2, C^6), 130.3 (CH_2=), 136.8 (=$CHSO_2$). Found, %: C 41.10; H 4.24. $C_9H_{11}BrO_2S$. Calculated, %: C 41.08; H 4.21.

Reaction of tricycloheptane 6 with an equimolar amount of sodium methoxide or sodium methanethiolate (*general procedure*). Compound **6**, 263 mg (1 mmol), was dissolved in 10 mL of anhydrous methanol, 2 mL of a 0.5 M solution of sodium methoxide or sodium methanethiolate in methanol was added, and the mixture was stirred for 5 h at 20°C. The solvent was removed under reduced pressure, the residue was dissolved in 15 mL of methylene chloride, and the solution was washed with water (2×5 mL) and dried over $MgSO_4$. The solvent was distilled off on a rotary evaporator, and the crystalline residue was analyzed by ^1H and ^{13}C NMR and purified by flash chromatography on silica gel.

7-Bromo-1-(2-methoxyethane-1-sulfonyl)tricyclo[4.1.0.0^{2,7}]heptane (7). Yield 221 mg (75%), mp 53–54°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3035 w, 2944 m, 1481 m, 1439 m, 1330 s (SO_2, asym.), 1212 m, 1141 v.s (SO_2, sym.), 1109 m, 753 s, 660 m. ^1H NMR spectrum, δ, ppm: 1.23–1.49 m (2H, 4-H), 1.65–1.87 m (4H, 3-H, 5-H), 2.91 br.s (2H, 2-H, 6-H), 3.18 s (3H, CH_3O), 3.37 t (2H, CH_2SO_2, J = 5.8 Hz), 3.78 t (2H, CH_2O, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.6 (C^3, C^5), 24.3 (C^4), 32.2 (C^7), 36.3 (C^1), 50.2 (C^2, C^6), 56.0 (CH_3O), 58.6 (CH_2SO_2), 65.5 (CH_2O). Found, %: C 41.71; H 5.14. $C_{10}H_{15}BrO_3S$. Calculated, %: C 40.69; H 5.12.

7-Bromo-1-[2-(methylsulfanyl)ethane-1-sulfonyl]tricyclo[4.1.0.0^{2,7}]heptane (8). Yield 235 mg (76%), mp 71–72°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3040 w, 2951 m, 1481 m, 1439 m, 1334 s (SO_2, asym.), 1215 m, 1142 v.s (SO_2, sym.), 1105 m, 753 s, 660 m. ^1H NMR spectrum, δ, ppm: 1.16–1.41 m (2H, 4-H), 1.52–1.72 m (4H, 3-H, 5-H), 2.53 br.s (2H, 2-H, 6-H), 2.12 s (3H, CH_3S), 3.61 t (2H, CH_2SO_2, J = 6.5 Hz), 2.98 t (2H, CH_2S, J = 6.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.0 (CH_3S), 19.3 (C^3, C^5), 23.5 (C^4), 26.1 (C^7), 28.5 (CH_2S), 35.2 (C^1), 38.0 (C^2, C^6), 58.7 (CH_2SO_2). Found, %: C 38.60; H 4.87. $C_{10}H_{15}BrO_2S_2$. Calculated, %: C 38.59; H 4.86.

Reaction of tricycloheptane 6 with 3 equiv of sodium methoxide or sodium methanethiolate (*general procedure*). Compound **6**, 263 mg (1 mmol), was dissolved in 10 mL of anhydrous methanol, 6 mL of a 0.5 M solution of sodium methoxide or sodium methanethiolate in methanol was added, and the mixture was heated in a sealed ampule at 90°C for 5 h. The ampule was cooled and opened, the solvent was removed under reduced pressure, the residue was dissolved in 15 mL of methylene chloride, and the solution was washed with water (2×5 mL) and dried over $MgSO_4$. The solvent was distilled off on a rotary evaporator, and the crystalline residue was analyzed by ^1H and ^{13}C NMR and purified by recrystallization.

6,6-Dimethoxy-7-*syn*-(2-methoxyethane-1-sulfonyl)bicyclo[3.1.1]heptane (9). Yield 215 mg (77%), mp 78–79°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3093 m, 2949 m, 1453 m, 1334 s (SO_2, asym.), 1267 m, 1210 m, 1133 v.s (SO_2, sym.), 1110 s, 1095 s, 1060 m, 883 m, 744 s, 657 m. ^1H NMR spectrum, δ, ppm: 1.49–1.61 m (1H, 3-*endo*-H), 1.65–1.76 m (1H, 3-*exo*-H), 1.80–1.90 m (2H, 2-*endo*-H, 4-*endo*-H), 2.03–2.14 m (2H, 2-*exo*-H, 4-*exo*-H), 3.07 br.s (2H, 1-H, 5-H), 3.15 s (3H, CH_3O), 3.31 s (3H, CH_3O), 3.20 t (2H, CH_2SO_2, J = 5.4 Hz), 3.79 t (2H, CH_2O, J = 5.4 Hz), 3.36 s (3H, CH_3O), 4.32 t (1H, 7-*anti*-H, J = 5.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.3 (C^3), 23.1 (C^2, C^4), 40.8 (C^1, C^5), 53.4 (CH_2SO_2), 55.9 (CH_3O), 56.5 (CH_3O), 66.1 (C^7), 58.8 (CH_3O), 59.7 (CH_2O), 73.2 (C^6). Found, %: C 53.22; H 8.11. $C_{11}H_{20}O_4S$. Calculated, %: C 53.20; H 8.12.

6,6-Bis(methylsulfanyl)-7-*syn*-[2-(methylsulfanyl)ethane-1-sulfonyl]bicyclo[3.1.1]heptane (10). Yield 274 mg (84%), mp 134–135°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 3095 m, 2951 m, 1454 m, 1330 s (SO_2, asym.), 1261 m, 1211 m, 1132 v.s (SO_2, sym.), 1138 s, 1091 s, 1061 m, 880 m, 740 s, 651 m. ^1H NMR spectrum, δ, ppm: 1.19–1.34 m (1H, 3-*endo*-H), 1.55–1.66 m (1H, 3-*exo*-H), 1.75–1.85 m (2H, 2-*endo*-H, 4-*endo*-H), 1.95–2.10 m (2H, 2-*exo*-H, 4-*exo*-H), 2.95 br.s (2H, 1-H, 5-H), 2.01 s (3H, CH_3S), 2.15 s (3H, CH_3S), 2.21 s (3H, CH_3S), 2.70 t (2H, CH_2S, J = 7.5 Hz), 3.19 t (2H, CH_2SO_2, J = 7.5 Hz), 3.35 t (1H, 7-*anti*-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.9 (C^3), 13.0 (CH_3S), 13.9 (CH_3S), 14.8 (CH_3S), 22.1 (C^2, C^4), 39.8 (C^1, C^5), 42.6 (CH_2S), 51.2 (CH_2SO_2), 65.1 (C^7), 63.0 (C^6). Found, %: C 44.16; H 6.77. $C_{12}H_{22}O_2S_4$. Calculated, %: C 44.14; H 6.79.

Reaction of tricycloheptanes 7 and 8 with 2 equiv of sodium methoxide or sodium methanethiolate (*general procedure*). Compound **7** or **8**, 0.5 mmol, was dissolved in 10 mL of anhydrous methanol, 2 mL of a 0.5 M solution of sodium methoxide or sodium methanethiolate in methanol was added, and the mixture was heated in a sealed ampule at 90°C for 5 h. The ampule was cooled and opened, the solvent was removed under reduced pressure, the residue was dissolved in 15 mL of methylene chloride, and the solution was washed with water (2×5 mL) and dried over $MgSO_4$. The solvent was distilled off on a rotary evaporator, and the crystalline residue was analyzed by ^1H and ^{13}C NMR.

CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

REFERENCES

1. Block, E. and Aslam, M., *J. Am. Chem. Soc*., 1983, vol. 105, p. 6164. https://doi.org/10.1021/ja00357a040
2. Block, E., Aslam, M., Eswarakrishnan, V., and Wall, A., *J. Am. Chem. Soc*., 1983, vol. 105, p. 6165. https://doi.org/10.1021/ja00357a041
3. Block, E., Eswarakrishnan, V., and Gebreyes, K., *Tetrahedron Lett*., 1984, vol. 25, p. 5469. https://doi.org/10.1016/s0040-4039(01)81601-4

4. Block, E., Aslam, M., Eswarakrishnan, V., Gebreyes, K., Hutchinson, J., Iyer, R., Laffitte, J.A., and Wall, A., *J. Am. Chem. Soc*., 1986, vol. 108, p. 4568. https://doi.org/10.1021/ja00275a051
5. Vasin, V.A., Kostryukov, S.G., Romanova, E.V., Bolusheva, I.Yu., and Razin, V.V., *Russ. J. Org. Chem*., 1996, vol. 32, p. 1649.
6. Vasin, V.A., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 2002, vol. 38, p. 1582–1587. https://doi.org/10.1023/A:1022597614806
7. Vasin, V.A., Kostryukov, S.G., Razin, V.V., Bolusheva, I.Yu., and Zefirov, N.S., *Zh. Org. Khim*., 1994, vol. 30, p. 1351.
8. Vasin, V.A., Korovin, D.Yu., Petrov, P.S., Razin, V.V., and Somov, N.V., *Russ. J. Org. Chem*., 2015, vol. 51, p. 1697. https://doi.org/10.1134/S1070428015120052
9. Marvel, C.S. and Bailey, C.F., *Org. Synth*., 1938, vol. 18, p. 77. https://doi.org/10.15227/orgsyn.018.0077
10. Vasin, V.A., Bolusheva, I.Yu., Chernyaeva, L.A., Surmina, L.S., and Zefirov, N.S., *Zh. Org. Khim*., 1990, vol. 26, p. 1509.
11. Vasin, V.A., Kostryukov, S.G., Razin, V.V., and Zefirov, N.S., *Zh. Org. Khim*., 1994, vol. 30, p. 680.
12. Silverstein, R.M., Webster, F.X., and Kiemle, D.J., *Spectrometric Identification of Organic Compounds*, Hoboken, NJ: Wiley, 2005, 7th ed.
13. Azran, C. and Hoz, S., *Tetrahedron*, 1995, vol. 51, p. 11421. https://doi.org/10.1016/0040-4020(95)00706-E
14. Szeimies, G., Philipp, F., Baumgärten, O., and Harnisch, J., *Tetrahedron Lett*., 1977, vol. 18, p. 2135. https://doi.org/10.1016/S0040-4039(01)83700-X