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Reactions of Tricyclo[4.1.0.0^{2,7}]heptane and 1-Methyltricyclo[4.1.0.0^{2,7}]heptane with 2-Bromoethanesulfonyl Bromide

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Abstract—2-Bromoethanesulfonyl bromide reacts with tricyclo[4.1.0.0^{2,7}]heptane and 1-methyltricyclo[4.1.0.0^{2,7}]heptane according to a radical mechanism to give products of both *anti* and *syn* addition across the C^1–C^7 central bicyclobutane bond having a norpinane (bicyclo[3.1.1]heptane) structure. Treatment of the adducts with triethylamine leads to the formation of vinyl sulfones as a result of 1,2-dehydrobromination, and their reaction with sodium methoxide involves 1,2- and 1,3-dehydrobromination and nucleophilic addition, depending on the substrate structure and reactant ratio.

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

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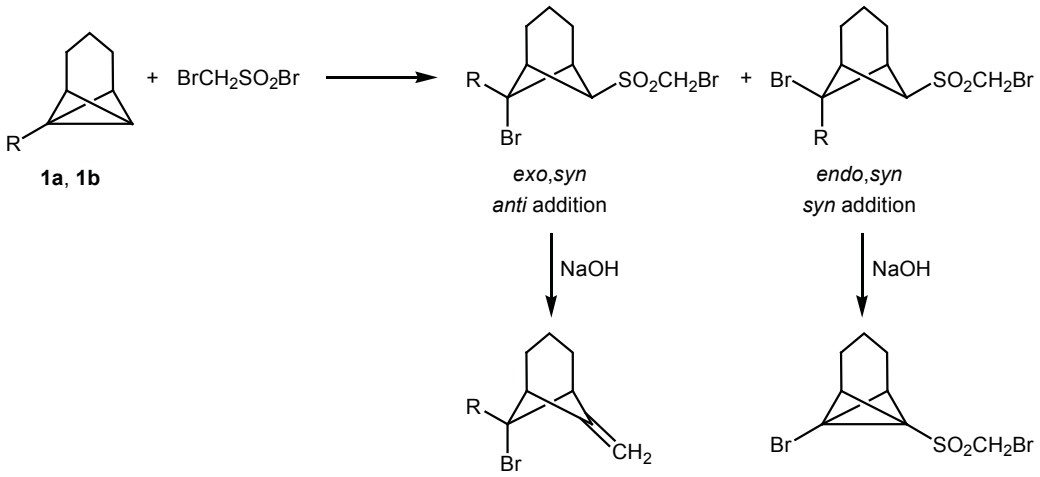
It is known [1–4] that bromomethanesulfonyl bromide reacts with alkene via addition to the C=C double bond with the formation of α,β′-dibromo sulfones which undergo dehydrobromination and desulfonation by the action of bases to give conjugated dienes. Bromomethanesulfonyl bromide reacted in a similar way with compounds **1a** and **1b** of the tricyclo[4.1.0.0^{2,7}]heptane series [5], affording the corresponding *anti*- and *syn*-addition products with a bicyclo[3.1.1]heptane (norpinane) structure and *endo* (*syn*) orientation of the bromomethanesulfonyl group. Treatment of the *anti* adducts with bases, e.g., sodium hydroxide in aqueous dioxane, led to the formation of 6-methylidenebicyclo[3.1.1]heptane derivatives as a result of Ramberg–Bäcklund reaction. Under similar conditions, *syn*-addition products are converted to 1-(bromomethanesulfonyl)tricyclo[4.1.0.0^{2,7}]heptanes via 1,3-dehydrobromination (Scheme 1) [5].

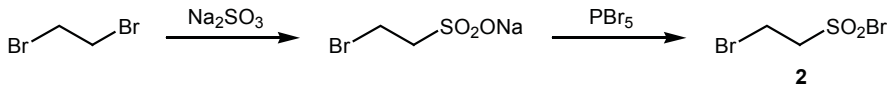
Thus, there is no doubt that halogen-substituted alkanesulfonyl bromides possess a high synthetic

Scheme 1.



R = H (**a**), Me (**b**).

Scheme 2.



potential as efficient reagents for the introduction of a haloalkanesulfonyl group and its further transformations.

With the goal of extending the series of available haloalkanesulfonyl halides, we have synthesized 2-bromoethanesulfonyl bromide (**2**) and studied its reactions with tricycloheptanes **1a** and **1b**. It should be noted that compound **2** has not been reported in the literature. To obtain sulfonyl bromide **2**, we used the procedure proposed previously for the synthesis of iodomethanesulfonyl bromide by treatment of the corresponding sodium sulfonate with phosphorus(V) bromide [4] (Scheme 2). Sodium 2-bromoethanesulfonate was prepared by reaction of excess 1,2-dibromoethane with sodium sulfite [6].

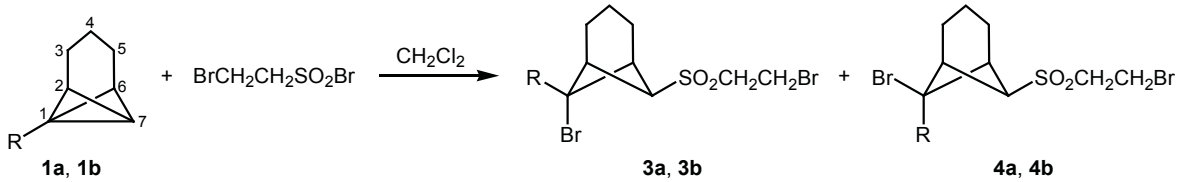
The reactions of tricyclo[4.1.0.0^{2,7}]heptanes **1a** and **1b** with sulfonyl bromide **2** were carried out by mixing the reactant in anhydrous methylene chloride at 0°C with addition of anhydrous sodium carbonate, followed by exposing the mixture to scattered sunlight at room temperature for up to 10 h until compound **2** disappeared completely according to the TLC data. In each case, products of addition of **2** across the C^1–C^7 bond of tricycloheptanes **1a** and **1b** with a bicyclo[3.1.1]-heptane structure were formed in high isolated yields as mixtures of two diastereoisomers **3** and **4**, where the *anti*-addition product (**3a** or **3b**) predominated (Scheme 3). According to the ^{1}H NMR spectra of the reaction mixtures, the isomer ratio **3a**/**4a** was 65:35, and the isomer ratio **3b**/**4b** was 85:15.

The individual stereoisomers were isolated by alumina column chromatography, and their structure and configuration were determined by ^{1}H and ^{13}C NMR spectroscopy. In particular, the bicyclo[3.1.1]-heptane skeleton of **3** and **4** was confirmed by the presence in their ^{13}C NMR spectra of five signals from seven carbon atoms with expected intensities at appropriate positions. The orientation of substituents was inferred by analysis of the positions and multiplicities of the 6-H and 7-H signals in the ^{1}H NMR spectra with account taken of correlations found previously for compounds of the norpinane series [7–9]. The triplet signal of 6-H in the spectra of **3a** and **4a** and of 7-H in the spectra of **3b** and **4b** indicated *anti* orientation of the corresponding proton with respect to the trimethylene bridge. Likewise, the *endo* orientation of 7-H in molecule **3a** followed from the singlet signal of that proton in the ^{1}H NMR spectrum. The IR spectra of **3** and **4** characteristically sowed strong absorption bands at ~1130 and ~1330 cm^{-1} due to symmetric and antisymmetric stretching vibrations of the sulfonyl group, respectively [10].

We can conclude that, as in the reactions with bromomethanesulfonyl bromide [5], arenesulfonyl halides [7, 9, 11], and some other sulfonyl derivatives [8], the addition of 2-bromoethanesulfonyl bromide to tricycloheptanes **1a** and **1b** involves exclusively the C^1–C^7 bond. Based on the data of [7–9], the described reaction should be assumed to follow a radical mechanism (Scheme 4), where (as in the other cases [5]) the reaction is initiated by the *endo* attack of sulfonyl radical. In the case of 1-methyltricyclo[4.1.0.0^{2,7}]-heptane (**1b**), this attack is completely regioselective and is directed at the more sterically accessible unsubstituted C^7 atom. The subsequent bromine atom transfer to bicyclo[3.1.1]heptyl intermediate occurs preferably in the *exo* position. As follows from the stereoisomer ratios (see above), the fraction of the *anti*-addition product increases in parallel with the volume of the R substituent on C^1.

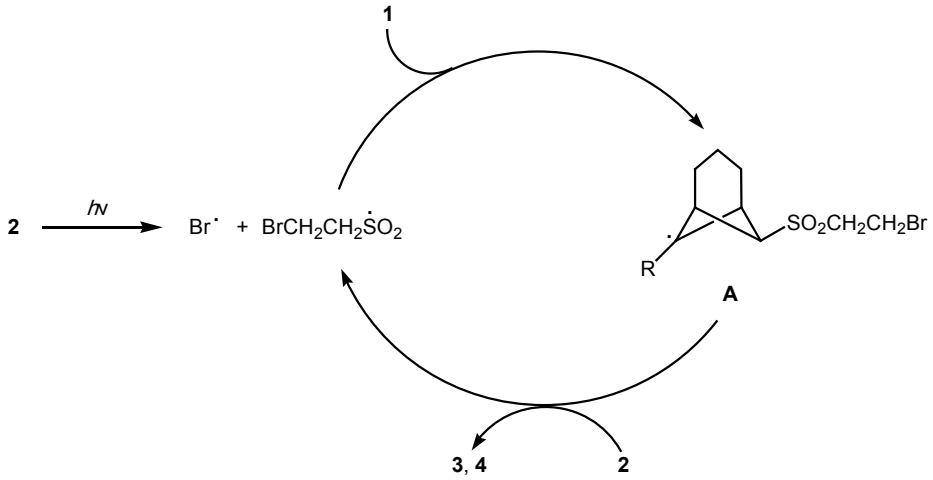
The 2-bromoethanesulfonyl moiety of compounds **3** and **4** is capable of undergoing various transformations by the action of nucleophiles and bases. *anti*-Addition products **3a** and **3b** readily reacted with an equimolar amount of triethylamine in benzene or sodium methox-

Scheme 3.



R = H (**a**), Me (**b**).

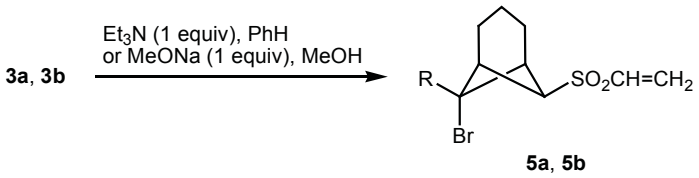
Scheme 4.



ide in methanol at 0°C to give vinyl sulfones **5a** and **5b** as a result of 1,2-dehydrobromination (Scheme 5). *syn*-Adducts **4a** and **4b** reacted with triethylamine in a similar way. However, their reaction with 1 equiv of sodium methoxide in methanol at 0°C led to the formation of a mixture of vinyl sulfone **6a** or **6b** and vinylsulfonyl-substituted tricycloheptane **7a** or **7b** (Scheme 6). According to the ^{1}H NMR spectra of the reaction mixtures, the product ratios **6a**/**7a** and **6b**/**7b** were 2.5:1 and 2.3:1, respectively. When 2 equiv of sodium methoxide was used, other conditions being equal, tricycloheptanes **7a** and **7b** were formed as the only products (Scheme 6).

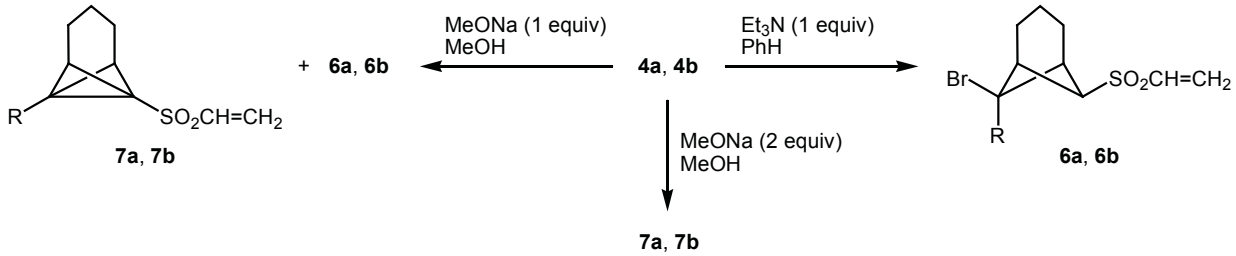
The reactions of **3a** and **3b** with 2 equiv of sodium methoxide in boiling methanol afforded compounds **8a** and **8b** (Scheme 7) with retention of the *exo*(*anti*)-oriented bromine atom. Obviously, compounds **8a** and **8b** were formed as a result of successive 1,2-dehydrobromination and nucleophilic addition of methoxide ion to the C=C bond of the vinylsulfonyl substituent. 2-Methoxyethyl sulfone **8a** was also obtained as the only product when compound **3a** was treated with 3 or 4 equiv of sodium methoxide. On the other hand, the reaction of **3b** with 3 equiv of sodium methoxide on heating in a sealed ampule (90°C) gave norpinane **9** (Scheme 8). The *exo* orientation of the sulfonyl group in molecule **9** was confirmed by the presence of a singlet of 6-*endo*-H in the ^{1}H NMR spectrum. The observed transformation involves 1,2-dehydrobromination of intermediately formed compound **8b** and subsequent epimerization at the carbon atom bearing the sulfonyl group. This result is not surprising since

Scheme 5.



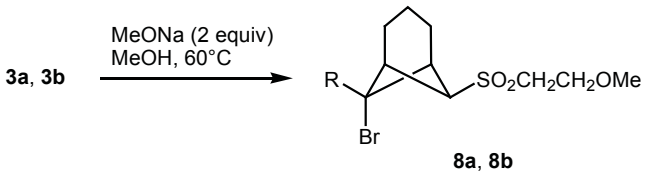
R = H (**a**), Me (**b**).

Scheme 6.



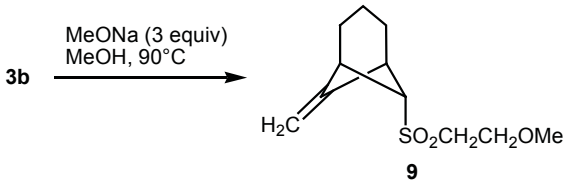
R = H (**a**), Me (**b**).

Scheme 7.



R = H (**a**), Me (**b**).

Scheme 8.



thermodynamic preference of *exo*(*anti*) orientation of the sulfonyl group in 6,7-disubstituted bicyclo[3.1.1]-heptanes was established in [12].

Sulfonyl-substituted tricycloheptanes **10a** and **10b** were formed in the reactions of **4a** and **4b** with 3 equiv of sodium methoxide (Scheme 9); compounds **10a** and **10b** are products of nucleophilic addition of methoxide ion to te double bond of the vinylsulfonyl fragment of intermediate tricycloheptanes **7a** and **7b**.

The higher reactivity of the vinylsulfonyl group of tricycloheptanes to nucleophilic attack in comparison to the C^1–C^7 bond was confirmed by quantum chemical calculations. The molecular geometry of tricycloheptane **7a** was fully optimized without symmetry constraints with account taken of solvent (methanol) effect according to the polarizable continuum model (PCM) [13]. The solvent parameters (dielectric constant and molecular radius) were taken from [14]. During geometry optimization, minima on the potential energy surface were localized by calculating normal vibration frequencies; the absence of imaginary frequencies in the vibrational spectrum of the optimized structure indicated that this structure corresponds to a minimum on the complete potential energy surface. The structures of the frontier molecular orbitals of tricycloheptane **7a** were calculated in the framework of the density functional theory (DFT) using B3LYP hybrid functional [13] and 6-311G standard basis set [15] included in Firefly software package [16]. Figure 1 shows that the lowest unoccupied molecular orbital (LUMO) of **7a**, at which nucleophilic attack is directed, is localized on the vinylsulfonyl fragment.

Compound **10b** proved to be resistant to further treatment with sodium methoxide due to steric shielding of the electrophilic center by methyl group on C^7. In contrast, by heating compound **4a** with 4 equiv of sodium methoxide in a sealed ampule (90°C) we obtained dimethoxy derivative **11** (Scheme 10) as a re-

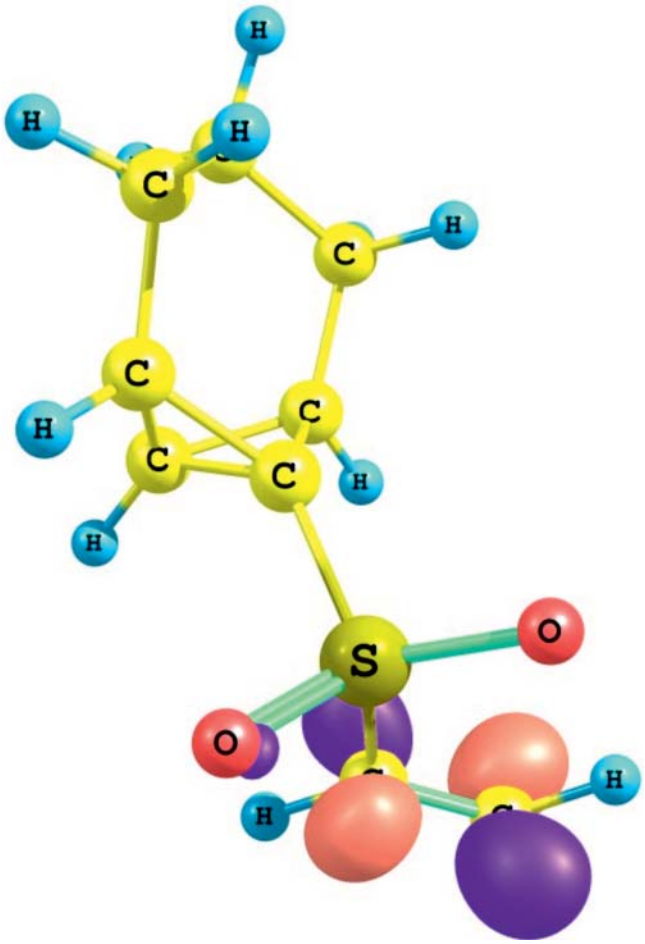
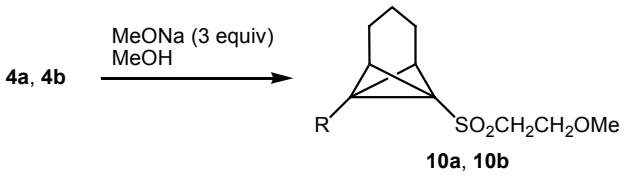


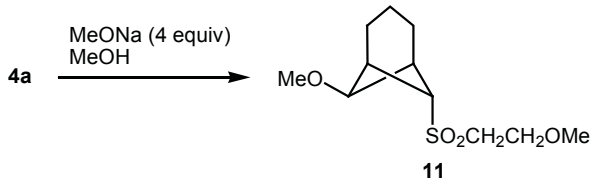
Fig. 1. Localization of the lowest unoccupied molecular orbital (LUMO) of compound **7a**.

Scheme 9.



R = H (**a**), Me (**b**).

Scheme 10.



sult of consecutive and concurrent 1,2- and 1,3-elimination reactions and subsequent nucleophilic addition to the double bond of the vinylsulfonyl fragment and C^1–C^7 bond. The *exo* orientation of the sulfonyl group in norpinane **11** is confirmed by the presence of a singlet signal of the 6-*endo*-H proton in the ^{1}H NMR spectrum.

All sulfones **5**–**11** were isolated in the pure state and were characterized by ^{1}H and ^{13}C NMR and IR spectra and elemental analyses.

Thus, 2-bromoethanesulfonyl bromide is a convenient reagent for the synthesis of diastereoisomeric 2-bromoethyl sulfones of the bicyclo[3.1.1]heptane series, which can be readily converted to vinyl sulfones, and the latter are capable of adding nucleophiles. Furthermore, 1,3-dehydrobromination of the *syn*-addition products gives 1-(vinylsulfonyl)tricyclo-[4.1.0.0^{2,7}]heptanes which can add nucleophiles both at the vinyl C=C bond and C^1–C^7 bicyclobutane bond.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Jeol JNM-ECX 400 spectrometer at 400 and 100 MHz, respectively; the chemical shifts were measured relative to the residual proton (δ 7.26 ppm) and carbon signals (δ_C 77.16 ppm) of the solvent. The IR spectra were recorded in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform. Elemental analysis was performed with a Vario MICRO CHNS analyzer. Analytical TLC was run on Silufol UV-245 plates using light petroleum ether–diethyl ether (1:1) as eluent; spots were visualized by treatment with iodine vapor or under UV light. Aluminum oxide of Brockmann activity grade II was used for column chromatography (light petroleum ether–diethyl ether, 3:1 to 2:1). The melting points were measured in sealed glass capillaries on an MP-50 melting point analyzer.

Tricyclo[4.1.0.0^{2,7}]heptane (**1a**) [17], 1-methyltricyclo[4.1.0.0^{2,7}]heptane (**1b**) [18], and sodium 2-bromoethanesulfonate [6] were synthesized according to reported procedures. The purity of tricycloheptanes **1a** and **1b** was 97–98% (GLC).

2-Bromoethanesulfonyl 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-bromoethanesulfonate, 51.7 g (0.12 mol) of PBr_5, 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. When the ice melted, the organic phase was separated and dried over $CaCl_2$, the solvent was removed under reduced pressure (10–20 mm), and the product was distilled under a pressure not exceeding 1 mm Hg to collect a fraction boiling at 80–90°C. This fraction was distilled once more. Yield 17 g (67.5%), 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 tricycloheptanes 1a and 1b with 2-bromoethanesulfonyl bromide (2) (*general procedure*). A solution of 10 mmol of tricycloheptane **1a** or **1b** in 15 mL of anhydrous methylene chloride containing 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 at 0°C for 1 h and then at room temperature until compound **2**

disappeared (TLC). The solvent was removed under reduced pressure, and the residue was analyzed by TLC and ^{1}H NMR. The main products were isolated by alumina column chromatography and crystallization.

7-*anti*-Bromo-6-*endo*-(2-bromoethanesulfonyl)-bicyclo[3.1.1]heptane (3a). Yield 1.64 g (47.5%), mp 112–113°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2955 m, 1454 m, 1308 s (SO_2, asym.), 1290 s, 1137 v.s (SO_2, sym.), 1025 m, 745 s, 690 s. ^{1}H NMR spectrum, δ, ppm: 1.71–1.80 m (1H, 3-*endo*-H), 1.84–1.94 m (1H, 3-*exo*-H), 1.99–2.11 m (2H, 2-*endo*-H, 4-*endo*-H), 2.49–2.57 m (2H, 2-*exo*-H, 4-*exo*-H), 3.08 br.d (2H, 1-H, 5-H), 3.45 t (2H, CH_2Br, J = 8.0 Hz), 3.65 t (2H, CH_2SO_2, J = 7.9 Hz), 4.10 s (1H, 7-*syn*-H), 4.27 t (1H, 6-*exo*-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.4 (C^3), 20.6 (CH_2Br), 25.0 (C^2, C^4), 48.7 (C^1, C^5), 51.2 (C^7), 57.0 (CH_2SO_2), 57.9 (C^6). Found, %: C 31.23; H 4.06. $C_9H_{14}Br_2O_2S$. Calculated, %: C 31.24; H 4.08.

7-*syn*-Bromo-6-*endo*-(2-bromoethanesulfonyl)-bicyclo[3.1.1]heptane (4a). Yield 1.03 g (29.7%), mp 99–100°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: 1.75–1.84 m (2H, 3-H), 1.98–2.08 m (2H, 2-*endo*-H, 4-*endo*-H), 2.35–2.44 m (2H, 2-*exo*-H, 4-*exo*-H), 3.00 br.d (2H, 1-H, 5-H), 3.39 t (2H, CH_2Br, J = 7.8 Hz), 3.40 t (1H, 7-*anti*-H, J = 5.7 Hz), 3.68 t (2H, CH_2SO_2, J = 8.0 Hz), 4.41 t (1H, 6-*exo*-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.5 (C^3), 20.7 (CH_2Br), 21.6 (C^2, C^4), 45.2 (C^1, C^5), 48.6 (C^7), 56.8 (C^6), 57.2 (CH_2SO_2). Found, %: C 31.29; H 4.11. $C_9H_{14}Br_2O_2S$. Calculated, %: C 31.24; H 4.08.

6-*exo*-Bromo-7-*syn*-(2-bromoethanesulfonyl)-6-*endo*-methylbicyclo[3.1.1]heptane (3b). Yield 2.54 g (70.5%), mp 126–127°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2963 m, 1456 m, 1308 s (SO_2, asym.), 1290 s, 1129 v.s (SO_2, sym.), 1027 m, 743 s, 681 s. ^{1}H NMR spectrum, δ, ppm: 1.45–1.55 m (1H, 3-*endo*-H), 1.57–1.69 m (1H, 3-*exo*-H), 1.92 s (3H, CH_3), 1.94–2.17 m (2H, 2-*endo*-H, 4-*endo*-H), 2.28–2.50 m (2H, 2-*exo*-H, 4-*exo*-H), 3.09 br.d (2H, 1-H, 5-H), 3.44 t (2H, CH_2Br, J = 7.9 Hz), 3.61 t (2H, CH_2SO_2, J = 7.9 Hz), 4.59 t (1H, 7-*anti*-H, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.3 (C^3), 20.6 (CH_2Br), 23.8 (C^2, C^4), 23.8 (CH_3), 53.4 (C^1, C^5), 57.1 (CH_2SO_2), 57.8 (C^7), 68.1 (C^6). Found, %: C 33.39; H 4.51. $C_{10}H_{16}Br_2O_2S$. Calculated, %: C 33.35; H 4.48.

6-*endo*-Bromo-7-*syn*-(2-bromoethanesulfonyl)-6-*exo*-methylbicyclo[3.1.1]heptane (4b). Yield 0.29 g (8.0%), mp 95–96°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2961 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: 1.72–1.83 m (1H, 3-*endo*-H), 1.87–1.96 m (1H, 3-*exo*-H), 2.12 s (3H, CH_3), 2.10–2.27 m (2H, 2-*endo*-H, 4-*endo*-H), 2.38–2.58 m (2H, 2-*exo*-H, 4-*exo*-H), 2.90 br.d (2H, 1-H, 5-H), 3.40 t (2H, CH_2Br, J = 8.0 Hz), 3.59 t (2H, CH_2SO_2, J = 7.9 Hz), 3.85 t (1H, 7-*anti*-H, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.7 (C^3), 20.5 (CH_2Br), 25.2 (C^2, C^4), 29.0 (CH_3), 51.2 (C^1, C^5), 54.4 (C^7), 57.2 (CH_2SO_2), 66.3 (C^6). Found, %: C 33.39; H 4.51. $C_{10}H_{16}Br_2O_2S$. Calculated, %: C 33.35; H 4.48.

Reaction of bicycloheptanes 3a, 3b, 4a, and 4b with triethylamine (*general procedure*). A solution of 0.069 mL (0.5 mmol) of triethylamine in 2 mL of anhydrous benzene was added to a solution of 0.5 mmol of compound **3a**, **3b**, **4a**, or **4b** in 5 mL of anhydrous benzene. The mixture was stirred for 1 h at 0°C, 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 ^{1}H and ^{13}C NMR and purified by crystallization.

7-*anti*-Bromo-6-*endo*-(ethenesulfonyl)bicyclo[3.1.1]heptane (5a). Yield 91 mg (68.6%), mp 98–99°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 3091 m, 2950 m, 1648 m (C=C), 1451 m, 1311 s (SO_2, asym.), 1291 s, 1142 v.s (SO_2, sym.), 1041 m, 746 s, 695 s. ^{1}H NMR spectrum, δ, ppm: 1.75–1.80 m (1H, 3-*endo*-H), 1.86–1.97 m (1H, 3-*exo*-H), 2.00–2.15 m (2H, 2-*endo*-H, 4-*endo*-H), 2.53–2.64 m (2H, 2-*exo*-H, 4-*exo*-H), 3.16 br.d (2H, 1-H, 5-H), 4.11 s (1H, 7-*syn*-H, J = 5.7 Hz), 4.47 t (1H, 6-*exo*-H, J = 5.8 Hz), 6.57 d.d (1H, CH_2=, J = 10.7, 1.8 Hz), 7.08 d.d (1H, CH_2=, J = 17.1, 1.8 Hz), 7.60 d.d (1H, SO_2CH=, J = 17.1, 10.7 Hz). ^{13} NMR spectrum, δ_C, ppm: 13.5 (C^3), 25.1 (C^2, C^4), 49.3 (C^1, C^5), 51.8 (C^7), 58.1 (C^6), 130.5 (CH_2=), 137.2 (=$CHSO_2$). Found, %: C 40.71; H 4.90. $C_9H_{13}BrO_2S$. Calculated, %: C 40.77; H 4.94.

7-*syn*-Bromo-6-*endo*-(ethenesulfonyl)bicyclo[3.1.1]heptane (6a). Yield 86 mg (65.0%), mp 81–82°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 3090 m, 2949 m, 1647 m (C=C), 1448 m, 1310 s (SO_2, asym.), 1295 s, 1139 v.s (SO_2, sym.), 1031 m, 745 s, 690 s. ^{1}H NMR spectrum, δ, ppm: 1.55–1.74 m (2H, 3-H), 1.78–1.98 m (2H, 2-*endo*-H, 4-*endo*-H), 2.15–

2.34 m (2H, 2-*exo*-H, 4-*exo*-H), 2.93 br.d (2H, 1-H, 5-H), 3.40 t (1H, 7-*anti*-H, J = 5.7 Hz), 4.56 t (1H, 6-*exo*-H, J = 5.8 Hz), 6.56 d.d (1H, CH_2=, J = 10.7, 1.8 Hz), 7.06 d.d (1H, CH_2=, J = 17.1, 1.8 Hz), 7.65 d.d (1H, SO_2CH=, J = 17.1, 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.5 (C^3), 20.7 (C^2, C^4), 44.8 (C^1, C^5), 47.2 (C^7), 55.4 (C^6), 130.5 (CH_2=), 137.1 (=$CHSO_2$). Found, %: C 40.71; H 4.90. $C_9H_{13}BrO_2S$. Calculated, %: C 40.77; H 4.94.

6-*exo*-Bromo-7-*syn*-(ethenesulfonyl)-6-*endo*-methylbicyclo[3.1.1]heptane (5b). Yield 94 mg (67.4%), mp 74–75°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 3092 m, 2959 m, 1644 m (C=C), 1452 m, 1314 s (SO_2, asym.), 1289 s, 1140 v.s (SO_2, sym.), 1037 m, 745 s, 680 s. ^1H NMR spectrum, δ, ppm: 1.65–1.75 m (1H, 3-*endo*-H), 1.80–1.90 m (1H, 3-*exo*-H), 2.13 s (3H, CH_3), 2.01–2.21 m (2H, 2-*endo*-H, 4-*endo*-H), 2.30–2.49 m (2H, 2-*exo*-H, 4-*exo*-H), 2.91 br.d (2H, 1-H, 5-H), 4.31 t (1H, 7-*anti*-H, J = 5.7 Hz), 6.61 d.d (1H, CH_2=, J = 10.7, 1.8 Hz), 7.10 d.d (1H, CH_2=, J = 17.1, 1.8 Hz), 7.63 d.d (1H, SO_2CH=, J = 17.1, 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.7 (C^3), 25.2 (C^2, C^4), 29.5 (CH_3), 51.9 (C^1, C^5), 54.3 (C^7), 65.3 (C^6), 129.9 (CH_2=), 138.0 (=$CHSO_2$). Found, %: C 43.06; H 4.47. $C_{10}H_{15}BrO_2S$. Calculated, %: C 43.02; H 5.42.

6-*endo*-Bromo-7-*syn*-(ethenesulfonyl)-6-*exo*-methylbicyclo[3.1.1]heptane (6b). Yield 94 mg (67.4%), mp 74–75°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 3089 m, 2956 m, 1646 m (C=C), 1453 m, 1310 s (SO_2, asym.), 1290 s, 1135 v.s (SO_2, sym.), 1040 m, 740 s, 686 s. ^1H NMR spectrum, δ, ppm: 1.70–1.80 m (1H, 3-*endo*-H), 1.83–1.94 m (1H, 3-*exo*-H), 2.10 s (3H, CH_3), 2.08–2.24 m (2H, 2-*endo*-H, 4-*endo*-H), 2.34–2.54 m (2H, 2-*exo*-H, 4-*exo*-H), 2.86 br.d (2H, 1-H, 5-H), 3.92 t (1H, 7-*anti*-H, J = 5.7 Hz), 6.57 d.d (1H, CH_2=, J = 10.7, 1.8 Hz), 7.08 d.d (1H, CH_2=, J = 17.1, 1.8 Hz), 7.60 d.d (1H, SO_2CH=, J = 17.1, 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.8 (C^3), 25.2 (C^2, C^4), 29.3 (CH_3), 51.4 (C^1, C^5), 54.3 (C^7), 66.5 (C^6), 130.8 (CH_2=), 138.9 (=$CHSO_2$). Found, %: C 43.06; H 4.47. $C_{10}H_{15}BrO_2S$. Calculated, %: C 43.02; H 5.42.

Reaction of bicycloheptanes 3a, 3b, 4a, and 4b with an equimolar amount of sodium methoxide (*general procedure*). Compound **3a**, **3b**, **4a**, or **4b**, 0.5 mmol, was dissolved in 10 mL of anhydrous methanol, 1 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, the solution was washed with water (2×5 mL) and dried over $MgSO_4$, and the solvent was distilled off on a rotary evaporator. The crystalline residue was analyzed by ^1H and ^{13}C NMR.

Reaction of bicycloheptanes 3a and 3b with 2 equiv of sodium methoxide (*general procedure*). Compound **3a** or **3b**, 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 refluxed with stirring for 1 h. The solvent was removed under reduced pressure, the residue was dissolved in 15 mL of methylene chloride, the solution was washed with water (2×5 mL) and dried over $MgSO_4$, and the solvent was distilled off on a rotary evaporator. The crystalline residue was analyzed by ^1H and ^{13}C NMR and then purified by crystallization.

7-*anti*-Bromo-6-*endo*-(2-methoxyethanesulfonyl)bicyclo[3.1.1]heptane (8a). Yield 96 mg (64.6%), mp 68–69°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2950 m, 2858 m, 1450 m, 1335 s (SO_2, asym.), 1261 m, 1215 m, 1133 v.s (SO_2, sym.), 1109 s, 1091 s, 1048 m, 749 s, 660 m. ^1H NMR spectrum, δ, ppm: 1.70–1.80 m (1H, 3-*endo*-H), 1.83–1.94 m (1H, 3-*exo*-H), 2.00–2.08 m (2H, 2-*endo*-H, 4-*endo*-H), 2.52–2.59 m (2H, 2-*exo*-H, 4-*exo*-H), 2.98 br.s (2H, 1-H, 5-H), 3.38 s (3H, CH_3O), 3.16 t (2H, CH_2SO_2, J = 5.4 Hz), 3.80 t (2H, CH_2O, J = 5.1 Hz), 4.09 s (1H, 7-*syn*-H), 4.38 t (1H, 6-*exo*-H, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.9 (C^3), 23.7 (C^2, C^4), 41.2 (C^1, C^5), 51.3 (CH_2SO_2), 57.9 (C^7), 58.8 (CH_3O), 59.6 (CH_2O), 63.2 (C^6). Found, %: C 40.43; H 5.76. $C_{10}H_{17}BrO_3S$. Calculated, %: C 40.41; H 5.77.

6-*exo*-Bromo-7-*syn*-(2-methoxyethanesulfonyl)-6-*endo*-methylbicyclo[3.1.1]heptane (8b). Yield 121 mg (78.0%), mp 139–140°C (from CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2950 m, 1453 m, 1330 s (SO_2, asym.), 1267 m, 1210 m, 1139 v.s (SO_2, sym.), 1110 s, 1093 s, 1059 m, 745 s, 659 m. ^1H NMR spectrum, δ, ppm: 1.34–1.49 m (1H, 3-*endo*-H), 1.53–1.64 m (1H, 3-*exo*-H), 1.92 s (3H, CH_3), 1.93–2.15 m (2H, 2-*endo*-H, 4-*endo*-H), 2.24–2.43 m (2H, 2-*exo*-H, 4-*exo*-H), 3.06 br.s (2H, 1-H, 5-H), 3.21 s (3H, CH_3O), 3.56 t (2H, CH_2SO_2, J = 4.8 Hz), 3.75 t (2H, CH_2O, J = 4.9 Hz), 4.56 t (1H, 7-*anti*-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.2 (C^3), 22.8 (C^2, C^4), 23.8 (CH_3), 52.3 (C^1, C^5), 57.2 (CH_3O), 57.3 (CH_2SO_2), 58.0 (C^7), 65.5 (CH_2O), 67.8 (C^6). Found, %: C 42.49; H 6.17. $C_{11}H_{19}BrO_3S$. Calculated, %: C 42.45; H 6.15.

Reaction of bicycloheptanes 4a and 4b with 2 equiv of sodium methoxide (*general procedure*). Compound **4a**, or **4b**, 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, the solution was washed with water (2×5 mL) and dried over $MgSO_4$, and the solvent was distilled off on a rotary evaporator. The crystalline residue was analyzed by ^{1}H and ^{13}C NMR and ten purified by crystallization.

1-(Ethenesulfonyl)tricyclo[4.1.0.0^{2,7}]heptane (7a). Yield 66 mg (72.0%), mp 55–56°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3090 w, 2950 m, 1642 m (C=C), 1485 m, 1450 m, 1331 s (SO_2, asym.), 1210 m, 1140 v.s (SO_2, sym.), 1120 m, 755 s, 661 m. ^{1}H NMR spectrum, δ, ppm: 1.21–1.48 m (2H, 4-H), 1.50–1.64 m (4H, 3-H, 5-H), 2.78 t (1H, 7-H, *J* = 3.0 Hz), 3.29 br.s (2H, 2-H, 6-H), 6.49 d.d (1H, CH_2=, *J* = 10.7, 1.8 Hz), 7.01 d.d (1H, CH_2=, *J* = 17.1, 1.8 Hz), 7.61 d.d (1H, SO_2CH=, *J* = 17.1, 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.6 (C^3, C^5), 20.1 (C^4), 21.8 (C^7), 30.4 (C^1), 49.0 (C^2, C^6), 130.3 (CH_2=), 136.8 (=$CHSO_2$). Found, %: C 58.70; H 6.54. $C_9H_{12}O_2S$. Calculated, %: C 58.67; H 6.56.

1-(Ethenesulfonyl)-7-methyltricyclo[4.1.0.0^{2,7}]-heptane (7b). Yield 70 mg (70.8%), mp 49–50°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3093 w, 2950 m, 1643 m (C=C), 1487 m, 1454 m, 1334 s (SO_2, asym.), 1215 m, 1143 v.s (SO_2, sym.), 1122 m, 760 s, 665 m. ^{1}H NMR spectrum, δ, ppm: 1.20–1.46 m (2H, 4-H), 1.47–1.60 m (4H, 3-H, 5-H), 1.91 s (3H, CH_3), 3.09 br.s (2H, 2-H, 6-H), 6.48 d.d (1H, CH_2=, *J* = 10.7, 1.8 Hz), 6.91 d.d (1H, CH_2=, *J* = 17.1, 1.8 Hz), 7.59 d.d (1H, SO_2CH=, *J* = 17.1, 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.1 (CH_3), 19.8 (C^3, C^5), 20.1 (C^4), 27.5 (C^7), 30.5 (C^1), 49.4 (C^2, C^6), 130.3 (CH_2=), 136.7 (=$CHSO_2$). Found, %: C 60.60; H 7.14. $C_{10}H_{14}O_2S$. Calculated, %: C 60.58; H 7.12.

Reaction of bicycloheptanes 3a and 3b with 3 equiv of sodium methoxide (*general procedure*). Compound **3a** or **3b**, 1 mmol, was dissolved in 10 mL of anhydrous methanol, 6 mL of a 0.5 M solution of sodium methoxide in methanol was added, and the mixture was heated at 90°C for 2 h in a sealed ampule. The ampule was cooled and opened, the solvent was removed under reduced pressure, the residue was dissolved in 20 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 product was analyzed by ^{1}H and ^{13}C NMR and purified by crystallization.

7-*anti*-Bromo-6-*endo*-(2-methoxyethanesulfonyl)-bicyclo[3.1.1]heptane (8a). Yield 180 mg (60.5%).

6-*exo*-(2-Methoxyethanesulfonyl)-7-methylidene-bicyclo[3.1.1]heptane (9). Yield 145 mg (63.0%), mp 94–95°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3095 m, 2950 m, 1660 m, 1451 m, 1332 s (SO_2, asym.), 1266 m, 1211 m, 1133 v.s (SO_2, sym.), 1117 s, 1090 s, 1059 m, 890 m, 749 s, 661 m. ^{1}H NMR spectrum, δ, ppm: 1.37–1.44 m (1H, 3-*endo*-H), 1.50–1.60 m (1H, 3-*exo*-H), 1.91–2.12 m (2H, 2-*endo*-H, 4-*endo*-H), 2.19–2.34 m (2H, 2-*exo*-H, 4-*exo*-H), 3.01 br.s (2H, 1-H, 5-H), 3.24 s (3H, CH_3O), 3.56 s (1H, 6-*endo*-H), 3.61 t (2H, CH_2SO_2, *J* = 4.9 Hz), 3.78 t (2H, CH_2O, *J* = 5.0 Hz), 5.09 s (2H, CH_2=). ^{13}C NMR spectrum, δ_C, ppm: 12.5 (C^3), 23.1 (C^2, C^4), 53.0 (C^1, C^5), 58.5 (CH_2SO_2), 58.1 (C^6), 59.4 (CH_3O), 65.5 (CH_2O), 115.6 (CH_2=), 130.1 (C^7). Found, %: C 57.34; H 7.81. $C_{11}H_{18}O_3S$. Calculated, %: C 57.36; H 7.88.

Reaction of bicycloheptanes 3a and 3b with 3 equiv of sodium methoxide (*general procedure*). Compound **4a** or **4b**, 0.5 mmol, was dissolved in 10 mL of anhydrous methanol, 3 mL of a 0.5 M solution of sodium methoxide in methanol was added, and the mixture was refluxed for 5 h with stirring. 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 product was analyzed by ^{1}H and ^{13}C NMR and then purified by crystallization.

1-(2-Methoxyethanesulfonyl)tricyclo[4.1.0.0^{2,7}]-heptane (10a). Yield 81 mg (74.9%), mp 48–49°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3095 w, 2856 m, 1451 m, 1332 s (SO_2, asym.), 1212 m, 1142 v.s (SO_2, sym.), 1120 m, 1091 s, 1058 m, 890 m, 665 m. ^{1}H NMR spectrum, δ, ppm: 1.32–1.51 m (2H, 4-H), 1.65–1.76 m (4H, 3-H, 5-H), 2.21 t (1H, 7-H, *J* = 3.0 Hz), 3.20 s (3H, CH_3O), 3.27 br.s (2H, 2-H, 6-H), 3.65 t (2H, CH_2SO_2, *J* = 5.1 Hz), 3.88 t (2H, CH_2O, *J* = 5.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.1 (C^3, C^5), 21.1 (C^4), 22.3 (C^7), 44.4 (C^1), 47.5 (C^2, C^6), 53.3 (CH_2SO_2), 58.8 (CH_3O), 59.7 (CH_2O). Found, %: C 55.59; H 7.44. $C_{10}H_{16}O_3S$. Calculated, %: C 55.53; H 7.46.

1-(2-Methoxyethanesulfonyl)-7-methyltricyclo-[4.1.0.0^{2,7}]heptane (10b). Yield 79 mg (68.7%),

mp 52–53°C (from Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3098 w, 2859 m, 1460 m, 1335 s (SO_2, asym.), 1210 m, 1146 v.s (SO_2, sym.), 1121 m, 1091 s, 1058 m, 890 m, 665 m. ^1H NMR spectrum, δ, ppm: 1.34–1.50 m (2H, 4-H), 1.55 s (3H, CH_3), 1.67–1.75 m (4H, 3-H, 5-H), 3.22 s (3H, CH_3O), 3.24 br.s (2H, 2-H, 6-H), 3.71 t (2H, CH_2O, J = 5.2 Hz), 3.58 t (2H, CH_2SO_2, J = 5.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.3 (C^3, C^5), 21.0 (C^4), 21.9 (CH_3), 27.5 (C^7), 44.8 (C^1), 47.5 (C^2, C^6), 52.7 (CH_2SO_2), 58.2 (CH_3O), 59.8 (CH_2O). Found, %: C 57.39; H 7.85. $C_{11}H_{18}O_3S$. Calculated, %: C 57.36; H 7.88.

Reaction of bicycloheptanes 3a, 3b, 4a, and 4b with 4 equiv of sodium methoxide (*general procedure*). Compound **3a**, **3b**, **4a**, or **4b**, 0.5 mmol, was dissolved in 10 mL of anhydrous methanol, 4 mL of a 0.5 M solution of sodium methoxide in methanol was added, and the mixture was heated at 90°C for 10 h in a sealed ampule. 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 product was analyzed by ^1H and ^{13}C NMR and then purified by crystallization.

7-*anti*-Bromo-6-*endo*-(2-methoxyethanesulfonyl)-bicyclo[3.1.1]heptane (8a). Yield 91 mg (61.3%).

7-*anti*-(2-Methoxyethanesulfonyl)-6-methylidenebicyclo[3.1.1]heptane (9). Yield 81 mg (70.4%).

1-(2-Methoxyethanesulfonyl)-7-methyltricyclo-[4.1.0.0^{2,7}]heptane (10b). Yield 75 mg (65.2%).

7-*syn*-Methoxy-6-*exo*-(2-methoxyethanesulfonyl)-bicyclo[3.1.1]heptane (11). Yield 81 mg (65.3%), mp 48–49°C (Et_2O–hexane). IR spectrum, ν, cm^{-1}: 3095 m, 2950 m, 1450 m, 1330 s (SO_2, asym.), 1262 m, 1204 m, 1130 v.s (SO_2, sym.), 1115 s, 1095 s, 1060 m, 883 m, 744 s, 657 m. ^1H NMR spectrum, δ, ppm: 1.50–1.62 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), 3.28 s (3H, CH_3O), 3.20 t (2H, CH_2O, J = 5.1 Hz), 3.79 t (2H, CH_2SO_2, J = 5.1 Hz), 3.36 s (3H, CH_3O), 3.35 s (1H, 6-*endo*-H), 4.32 t (1H, 7-*anti*-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.3 (C^3), 23.0 (C^2, C^4), 40.8 (C^1, C^5), 53.3 (CH_2SO_2), 55.8 (CH_3O), 66.0 (C^6), 58.8 (CH_3O), 59.6 (CH_2O), 73.2 (C^7). Found, %: C 53.22; H 8.11. $C_{11}H_{20}O_4S$. Calculated, %: C 53.20; H 8.12.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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