Unusual heterocyclisation in the transformation of 6-halomethylsulfonyl-substituted bicyclo[3.1.1]heptane under Ramberg–Bäcklund reaction conditions

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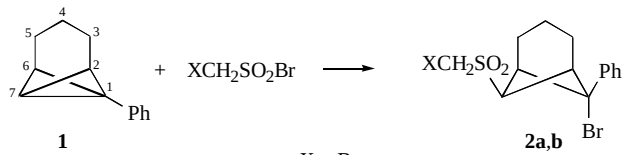
Boiling of *exo*-6-bromo-*syn*-7-bromo(chloro)methylsulfonyl-*endo*-6-phenylbicyclo[3.1.1]heptane in water–dioxane solutions of NaOH results in *anti*-6-hydroxy-7-methylene-*syn*-6-phenylbicyclo[3.1.1]heptane according to the Ramberg–Bäcklund reaction; in addition, a product of unusual heterocyclisation is formed, namely, 3-oxa-2-phenyl-5-thiatricyclo[4.4.0.0^{2,7}]decane *S*,*S*-dioxide.

The addition of bromomethylsulfonyl bromide to alkenes followed by treatment of the product with a base is a convenient modification of the Ramberg–Bäcklund reaction for the synthesis of conjugated dienes.[1] We believe that the application of a similar treatment to tricyclo[4.1.0.0^{2,7}]heptanes is also interesting from the synthetic viewpoint. In the present work, we studied these possibilities by performing the synthesis of adducts of bromo- and chloromethylsulfonyl bromides with 1-phenyltricyclo[4.1.0.0^{2,7}]heptane **1** and their transformations under Ramberg–Bäcklund reaction conditions.

Bromo- and chloromethylsulfonyl bromides reacted with compound **1** in CH_2Cl_2 at 0 °C similarly to phenylsulfonyl bromide[2] and were added *endo*, *anti*-stereoselectively only to the central bicyclobutane bond C(1)–C(7) to give adducts **2a** and **2b**, respectively (Scheme 1).†

The structure of compounds **2a**,**b**, including their configuration, was confirmed by ^{1}H and ^{13}C NMR spectra.‡ The *endo*-configuration of the sulfonyl group is supported by the H(7) signal shape (triplet, J = 7 Hz);[3] the orientation accepted for substituents at C(6) is confirmed by the high chemical shift of H(7) and by the presence of a high-field signal of the *endo*-H(3) atom, which is located in the screening region of the aromatic moiety (*cf.* ref. 4).



1 **2a**,**b**

a X = Br
b X = Cl

Scheme 1

Boiling of dibromide **2a** in a water–dioxane solution of NaOH resulted in the formation of two products, which contained no halogen atoms, in the ratio 1:2. In addition, the minor component contained no sulfur and was found to be a methylenehydroxy derivative of norpinane **3**, while the major component had the structure of an oxatricyclic sulfone **4**. The structures of compounds **3** and **4** were convincingly confirmed by ^{13}C NMR spectroscopic data.‡ To prove unambiguously the structure of sulfone **4**, we performed an X-ray diffraction study, see Figure 1.§

Chlorobromide **2b** was transformed almost completely to oxatricyclic sulfone **4** on treatment with a water–dioxane solution of NaOH.

In order to reveal methods for the formation of compounds **3** and **4**, the action of other bases/nucleophiles on dibromide **2a** was studied.¶ For example, heating of compound **2a** in aqueous THF in the presence of Na_2CO_3 resulted in the replacement of bromine at C(6) by a hydroxyl group. The hydrolysis occurred with almost complete retention of the configuration and produced alcohol **5**. The solvolysis of compound **2a** by treatment with sodium methoxide in methanol also occurred stereoselectively and gave ether **6**. A similar stereochemistry of

† Conditions of analytical TLC: Silufol UV-254 as the adsorbent; hexane–diethyl ether (1:1) as the eluent. The chromatograms were visualised in an iodine chamber. Column chromatography was carried out on L 40/100 μ silica gel or on Al_2O_3 (II activity grade) using light petroleum ether–diethyl ether [(2–3):1] as the eluent.

1-*Phenyltricyclo*[4.1.0.0^{2,7}]*heptane* **1** was obtained according to the reported procedure.[4a] Mp 72–74 °C (2 mmHg).

Bromo- and chloromethylsulfonyl bromides were synthesised according to procedures known from the literature.[1a] Compounds with 97–98% purity (GLC) were used in the reactions.

anti-6-*Bromo*-endo-7-*bromomethylsulfonyl*-syn-6-*phenylbicyclo*[3.1.1]-*heptane* **2a**. A powder of $CaCO_3$ (0.1 g) was added to a solution of $BrCH_2SO_2Br$ (2.38 g) in 5 ml of anhydrous CH_2Cl_2, then a solution of tricycloheptane **1** (1.70 g) in 5 ml of CH_2Cl_2 was added with cooling to –5 °C. The reaction mixture was kept at 0 °C for 14 h. The disappearance of the starting reagents was monitored by TLC. The solvent was evaporated *in vacuo*; the solid residue was crystallised from a CH_2Cl_2–hexane mixture (1:3) to give 1.24 g (yield 30.3%) of compound **2a**, mp 158–159 °C. Found (%): C, 41.34; H, 3.89. Calc. for $C_{14}H_{16}Br_2O_2S$ (%): C, 41.20; H, 3.95.

endo-7-*Bromomethylsulfonyl*-anti-6-*chloro*-syn-6-*phenylbicyclo*[3.1.1]-*heptane* **2b**. The reaction of $ClCH_2SO_2Br$ (1.14 g) and tricycloheptane **1** (1.00 g) in 5 ml of anhydrous CH_2Cl_2 was carried out at 0 °C for 10 h as indicated above. The procedure gave 1.49 g (yield 69%) of compound **2b**, mp 130–131 °C (CH_2Cl_2–hexane). Found (%): C, 46.31; H, 4.38. Calc. for $C_{14}H_{16}ClO_2S$ (%): C, 46.41; H, 4.45.

‡ ^{1}H and ^{13}C NMR spectra were recorded for solutions of compounds in $CDCl_3$ on a Bruker AM 200 spectrometer.

2a: ^{1}H NMR, δ: 3.67 [2H, H(1) and H(5)], 2.50–2.72 [m, 2H, *endo*-H(2) and *endo*-H(4)], 2.10–2.32 [m, 2H, *exo*-H(2) and *exo*-H(4)], 1.40–1.65 [m, 1H, *endo*-H(3)], 0.60–0.85 [m, 1H, *exo*-H(3)], 4.80 [t, 1H, H(7)], 4.39 (s, 2H, CH_2SO_2), 7.25–7.50 (m, 5H, Ph); ^{13}C NMR, δ: 52.4 [C(1) and C(5)], 23.4 [C(2) and C(4)], 12.2 [C(3)], 70.6 [C(6)], 57.2 [C(7)], 43.2 (CH_2SO_2), 125.0 (s, Ph), 127.9 (m, Ph), 128.6 (s, Ph), 140.0 (w, Ph).

2b: ^{1}H NMR, δ: 3.67 [2H, H(1) and H(5)], 2.50–2.72 [m, 2H, *endo*-H(2) and *endo*-H(4)], 2.10–2.32 [m, 2H, *exo*-H(2) and *exo*-H(4)], 1.40–1.65 [m, 1H, *endo*-H(3)], 0.55–0.85 [m, 1H, *exo*-H(3)], 4.78 [t, 1H, H(7)], 4.50 (s, 2H, CH_2SO_2), 7.15–7.48 (m, 5H, Ph); ^{13}C NMR, δ: 52.2 [C(1) and C(5)], 23.5 [C(2) and C(4)], 12.2 [C(3)], 70.8 [C(6)], 56.9 and 57.6 [C(7) and CH_2SO_2, signal assignements can be reversed], 125.1 (s, Ph), 128.0 (m, Ph), 128.6 (s, Ph), 140.0 (w, Ph).

3: ^{1}H NMR, δ: 3.26 [2H, H(1) and H(5)], 2.00–2.26 [m, 4H, *endo*-H(2), *exo*-H(2), *endo*-H(4) and *exo*-H(4)], 1.38–1.65 [m, 1H, *endo*-H(3)], 0.90–1.18 [m, 1H, *exo*-H(3)], 2.40 (br s., 1H, OH), 5.10 (s, 2H, CH_2=), 7.27–7.53 (5H, Ph); ^{13}C NMR, δ: 53.0 [C(1) and C(5)], 30.5 [C(2) and C(4)], 14.9 [C(3)], 78.9 [C(6)], 154.3 [C(7)], 102.7 (CH_2=), 126.9 (s, Ph), 127.3 (m, Ph), 128.6 (s, Ph), 139.7 (w, Ph).

4 (for convenience of comparison of ^{1}H and ^{13}C NMR spectra, non-systematic numbering of the framework of the compounds was used): ^{1}H NMR, δ: 3.61 [s, 2H, H(1) and H(5)], 1.98–2.25 [m, 4H, *endo*-H(2), *exo*-H(2), *endo*-H(4) and *exo*-H(4)], 1.35–1.58 [m, 1H, *endo*-H(3)], 0.92–1.21 [m, 1H, *exo*-H(3)], 3.32 [s, 1H, H(7)], 5.08 (s, 2H, CH_2SO_2), 7.18–7.32 and 7.32–7.50 (m, 2H and 3H, Ph); ^{13}C NMR, δ: 45.2 [C(1) and C(5)], 27.2 [C(2) and C(4)], 13.5 [C(3)], 88.3 [C(6)], 62.3 [C(7)], 80.1 (CH_2SO_2), 126.0 (s, Ph), 128.6 (m, Ph), 128.8 (s, Ph), 136.4 (w, Ph).

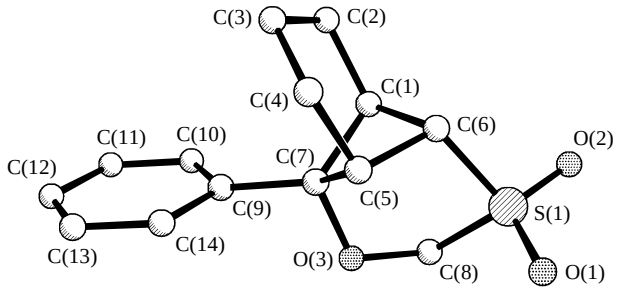


Figure 1 The structure of compound **4**, hydrogen atoms are omitted. Bond lengths (Å): C(1)–C(2) 1.524(3), C(1)–C(6) 1.554(3), C(1)–C(7) 1.552(3), C(2)–C(3) 1.525(3), S(1)–C(6) 1.771(2), S(1)–C(8) 1.800(2), O(3)–C(8) 1.407(3), O(3)–C(7) 1.466(2), C(7)–C(9) 1.503(3), C(9)–C(10) 1.381(3), C(10)–C(11) 1.392(4), C(11)–C(12) 1.373(4). Bond angles (°): O(1)–S(1)–C(6) 110.95(10), O(1)–S(1)–C(8) 109.99(12), C(6)–S(1)–C(8) 97.71(11), C(2)–C(1)–C(7) 112.9(2), C(2)–C(1)–C(6) 108.0(2), C(7)–C(1)–C(6) 85.8(2), C(1)–C(2)–C(3) 112.7(2), C(2)–C(3)–C(4) 113.1(2), C(1)–C(6)–S(1) 110.26(14), O(3)–C(7)–C(9), 105.40(14), O(3)–C(7)–C(1) 112.2(2), C(8)–O(3)–C(7) 116.9(2), C(9)–C(7)–C(1) 122.7(2), O(3)–C(8)–S(1) 109.3(2), O(1)–S(1)–O(2) 117.79(10).

nucleophilic substitution in benzyl halides to simulate halide **2a** has been reported previously.[2] It may be noted that the ^{1}H NMR spectra of compounds **5** and **6**, as well as those of **2a**,**b**, **3** and **4**, contain a one-proton high-field signal of *endo*-H(3) indicating a *syn*-orientation of the phenyl group in these compounds.

Boiling of alcohol **5** in a water–dioxane solution of NaOH resulted in a mixture of compounds **3** and **4** in the ratio 1:2. Similar treatment of ether **6** resulted in a methylenic derivative of norpinane **7**, whose ^{1}H and ^{13}C NMR spectra had the anticipated similarity with those of methylenehydroxy derivative **3**. Finally, treatment of ether **6** with potassium *tert*-butoxide in THF at 0 °C gave episulfone **8**,[††] which underwent thermal desulfonation on heating to give methylenenorpinane **7**.[‡‡] The presence of an episulfone fragment in compound **8** was detected on the basis of its ^{1}H and ^{13}C NMR spectra[§§] and the data for model compounds.[6] In order to confirm reliably the structure of episulfone **8**, an X-ray diffraction study was carried out, see Figure 2.[¶¶] A noteworthy feature of the structure of compound **3** is the increased length of the C(6)–C(8) bond (1.592 Å), which is typical of episulfones.[5a,7]

The transformations of dibromide **2a** carried out by treatment with bases/nucleophiles are presented in Scheme 2.

§ *X-Ray diffraction data*: crystals of $C_{14}H_{16}O_3S$ **4** are rhombic, space group *Pbca*. M = 264.33, T = 293(2) K, a = 7.396(2) Å, b = 11.491(4) Å, c = 29.382(9) Å, V = 2497(1) Å^3, crystal size 0.40×0.20×0.10 mm, Z = 8, d_{calc} = 1.406 g cm^{-3}, $F(000)$ = 1120, graphite monochromator, MoKα irradiation, λ = 0.71073 Å, μ = 0.256 mm^{-1}. The intensities of 2208 independent reflections were measured on a Siemens P3/PC diffractometer (θ–2θ scanning, $2\vartheta_{max}$ = 50°). The structure was solved by a direct method using the SHELXTL PLUS 5.0 program package.[13] The positions of the hydrogen atoms were revealed by difference synthesis of the electron density. Refinement of F^2 over 227 parameters in an anisotropic approximation (isotropic for H atoms) by the full-matrix least squares method for 1971 reflections was carried out to R_1 = 0.0419 [for 1646 reflections with $F > 4\sigma(F)$], wR_2 = 0.1004, S = 1.175. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Communications*, 1998, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/24.

¶ 7-*Methylene*-anti-6-*hydroxy*-syn-6-*phenylbicyclo*[3.1.1]*heptane* **3** and 2-*phenyl*-3-*oxa*-5-*thiatricyclo*[4.4.0.0^{2,7}]*decane S,S-dioxide* **4**. Compound **2a** (0.6 g) was added to a solution of NaOH (0.35 g) in 9 ml of dioxane diluted with water (1:1). The mixture was refluxed for 2 h, cooled and extracted with ether (5×8 ml). The ethereal extracts were dried with $MgSO_4$. The solvent was distilled off *in vacuo*, and the solid residue was chromatographed on a column with silica gel to give 60 mg (yield 20.7%) of compound **3** as an oil and 0.25 g (64.1%) of crystalline compound **4**.

Methylene derivative **3**, R_f 0.46. Found (%): C, 83.98, H, 8.11. Calc. for $C_{14}H_{16}O$ (%): C, 83.96; H, 8.05.

Tricyclic sulfone **4**, R_f 0.14. Mp 162–163 °C (hexane–diethyl ether, 2:1). Found (%): C, 63.63, 63.62; H, 6.12, 6.20. Calc. for $C_{14}H_{16}O_3S$ (%): C, 63.61; H, 6.10.

†† The isolation of episulfones under Ramberg–Bäcklund reaction conditions has been reported previously.[5]

‡‡ endo-7-(*Bromomethyl*)*sulfonyl*-anti-6-*hydroxy*-syn-6-*phenylbicyclo*[3.1.1]-*heptane* **5**. A solution of bromide **2a** (0.8 g) in 32 ml of THF diluted with water (32 ml) was refluxed for 1 h in the presence of sodium carbonate (1 g), cooled and extracted with ether (5×8 ml). The ethereal extracts were dried with $MgSO_4$ and the solvent was evaporated. Crystallisation from a chloroform–hexane mixture (1:3) gave 0.63 g (yield 92.9%) of carbinol **5** with mp 149–150 °C. Found (%): C, 48.58, H, 5.09. Calc. for $C_{14}H_{17}BrO_3S$ (%): C, 48.70; H, 4.96.

endo-7-(*Bromomethyl*)*sulfonyl*-anti-6-*methoxy*-syn-*phenylbicyclo*[3.1.1]-*heptane* **6**. Bromide **2a** (1.00 g) was added to a solution of sodium methoxide prepared from metallic sodium (0.08 g) and dry methanol (20 ml). The mixture was refluxed for 1.5 h in an inert atmosphere, cooled and neutralised with a methanolic solution of HCl using Thymol Blue as a pH indicator. The methanol was evaporated *in vacuo* and the residue was chromatographed on a column with Al_2O_3 to give 0.78 g (yield 89%) of compound **6**, mp 135–136 °C (CH_2Cl_2–hexane, 1:3). R_f 0.32. Found (%): C, 50.24, H, 5.26. Calc. for $C_{14}H_{17}BrO_3S$ (%): C, 50.15; H, 5.33.

Reaction of carbinol **5** *with sodium hydroxide*. A solution of carbinol **5** (0.20 g) and NaOH (0.14 g) in 10 ml of dioxane diluted with water (1:1) was refluxed for 1.5 h. The mixture was then treated as described above to give 0.11 g of a mixture of compounds **3** and **4**, whose composition is close to that obtained in the experiment with adduct **2a** (TLC and NMR monitoring).

Reaction of ester **6** *with sodium hydroxide*. Ester **6** (0.92 g) was mixed with a solution of NaOH (0.61 g) in 40 ml of dioxane diluted with water (1:1), and the mixture was refluxed for 3.5 h. The reaction mixture was cooled and extracted with CH_2Cl_2 (4×10 ml). The extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was distilled *in vacuo* to give 0.524 g (yield 98%) of methylenic derivative **7**, bp 73–74 °C (1 mmHg), R_f 0.85. Found (%): C, 84.13, H, 8.39. Calc. for $C_{15}H_{18}O$ (%): C, 84.07; H, 8.47.

anti-7-*Methoxy*-syn-7-*phenylbicyclo*[3.1.1]*heptyl*-6-*spiro*-1′-*thiacyclopropane S,S-dioxide* **8**. A powder of potassium *tert*-butoxide (0.89 g) was added with stirring in an inert atmosphere and cooling on an ice bath to a solution of ester **6** (1.90 g) in 14 ml of dry THF. The reaction mixture was stirred at 0 °C for 2 h, then filtered through a layer of Al_2O_3 (1 cm). The precipitate on the filter was washed with THF (5 ml) and the solvent was evaporated *in vacuo*. The solid residue was chromatographed on a column with Al_2O_3 to give 0.08 g of methylene derivative **7**, 0.35 g of episulfone **8** and 0.90 g of unreacted ester **6**.

Episulfone **8**. Mp 103–104 °C (CH_2Cl_2–hexane, 1:2), R_f 0.18. Found (%): C, 65.01, H, 6.77. Calc. for $C_{15}H_{18}O_3S$ (%): C, 64.72; H, 6.52.

Thermal decomposition of episulfone **8**. A solution of compound **8** (0.14 g) in dioxane (5 ml) was refluxed for 1 h. After removal of the solvent, methylene derivative **7** was obtained (0.06 g, yield 56.1%).

§§ **5**: ^{1}H NMR, δ: 3.32 [2H, H(1) and H(5)], 2.44–2.69 [m, 2H, *endo*-H(2) and *endo*-H(4)], 1.90–2.12 [m, 2H, *exo*-H(2) and *exo*-H(4)], 1.41–1.67 [m, 1H, *endo*-H(3)], 0.65–0.95 [m, 1H, *exo*-H(3)], 4.53 [t, 1H, H(7)], 4.33 (s, 2H, CH_2SO_2), *ca*. 2.0 (s, 1H, OH), 7.22–7.35 and 7.35–7.50 (m, 2H and 3H, Ph); ^{13}C NMR, δ: 49.2 [C(1) and C(5)], 22.6 [C(2) and C(4)], 12.7 [C(3)], 80.0 [C(6)], 55.8 [C(7)], 43.1 (CH_2SO_2), 125.3 (s, Ph), 128.0 (m, Ph), 128.9 (s, Ph), 139.3 (w, Ph).

6: ^{1}H NMR, δ: 3.42 [2H, H(1) and H(5)], 2.45–2.68 [m, 2H, *endo*-H(2) and *endo*-H(4)], 1.85–2.08 [m, 2H, *exo*-H(2) and *exo*-H(4)], 1.38–1.65 [m, 1H, *endo*-H(3)], 0.60–0.90 [m, 1H, *exo*-H(3)], 4.35 [t, 1H, H(7)], 4.34 (s, 2H, CH_2SO_2), 2.99 (s, 3H, OMe), 7.15–7.30 and 7.32–7.48 (m, 2H and 3H, Ph); ^{13}C NMR, δ: 46.0 [C(1) and C(5)], 22.5 [C(2) and C(4)], 12.9 [C(3)], 84.7 [C(6)], 56.3 [C(7)], 43.1 (CH_2SO_2), 50.5 (OMe), 127.0 (s, Ph), 128.0 (m, Ph), 128.1 (s, Ph), 135.0 (w, Ph).

7: ^{1}H NMR, δ: 3.30 [s, 2H, H(1) and H(5)], 2.10 [t, 4H, *endo*-H(2), *exo*-H(2), *endo*-H(4) and *exo*-H(4)], 1.35–1.57 [m, 1H, *endo*-H(3)], 0.82–1.06 [m, 1H, *exo*-H(3)], 2.96 (s, 3H, OMe), 4.93 (s, 2H, CH_2=), 7.18–7.28 and 7.28–7.48 (m, 2H and 3H, Ph); ^{13}C NMR, δ: 49.2 [C(1) and C(5)], 30.5 [C(2) and C(4)], 14.8 [C(3)], 84.0 [C(6)], 155.4 [C(7)], 50.3 (OMe), 100.6 (CH_2=), 127.3 (s, Ph), 127.9 (m, Ph), 128.3 (s, Ph), 136.4 (w, Ph).

8: ^{1}H NMR, δ: 3.25 [s, 2H, H(1) and H(5)], 1.90–2.20 [m, 4H, *endo*-H(2), *exo*-H(2), *endo*-H(4) and *exo*-H(4)], 1.18–1.40 [m, 1H, *endo*-H(3)], 0.80–1.04 [m, 1H, *exo*-H(3)], 2.92 (s, 2H, CH_2SO_2), 3.08 (s, 3H, OMe), 7.16–7.28 and 7.28–7.48 (m, 2H and 3H, Ph); ^{13}C NMR, δ: 43.9 [C(1) and C(5)], 23.6 [C(2) and C(4)], 13.3 [C(3)], 81.0 [C(6)], 56.4 [C(7)], 37.0 (CH_2SO_2), 50.8 (OMe), 126.9 (s, Ph), 127.9 (m, Ph), 128.8 (s, Ph), 135.3 (w, Ph).

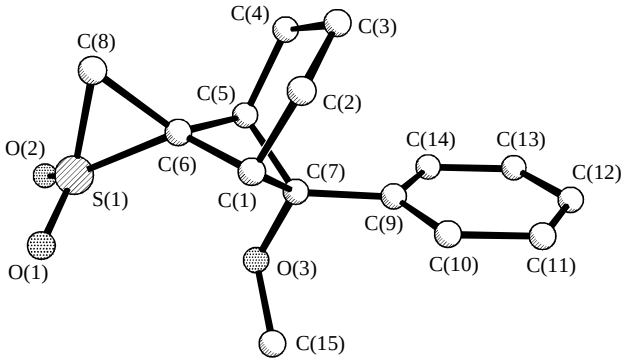
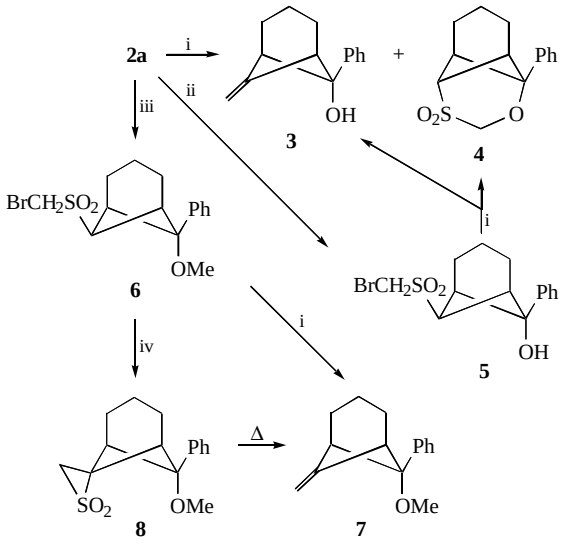


Figure 2 The structure of compound **8**, hydrogen atoms are omitted. Bond lengths (Å): C(1)–C(2) 1.533(3), C(1)–C(6) 1.520(2), C(1)–C(7) 1.571(3), C(2)–C(3) 1.519(3), C(3)–C(4) 1.536(4), C(6)–C(8) 1.592(3), S(1)–C(6) 1.715(2), S(1)–C(8) 1.735(2), S(1)–O(1) 1.436(2), O(3)–C(7) 1.436(2), O(3)–C(15) 1.416(3), C(7)–C(9) 1.504(2), C(9)–C(10) 1.396(3), C(10)–C(11) 1.388(3), C(11)–C(12) 1.380(3). Bond angles (°): O(2)–S(1)–O(1) 118.97(10), O(1)–S(1)–C(6) 116.36(9), O(1)–S(1)–C(8) 116.50(11), C(6)–S(1)–C(8) 54.94(9), C(15)–O(3)–C(7) 116.2(2), C(6)–C(1)–C(2) 107.3(2), C(6)–C(1)–C(7) 85.54(13), C(2)–C(1)–C(7) 111.8(2), C(3)–C(2)–C(1) 112.6(2), C(2)–C(3)–C(4) 114.4(2), C(1)–C(6)–C(5) 89.23(13), C(1)–C(6)–C(8) 127.0(2), C(1)–C(6)–S(1) 124.82(12), C(8)–C(6)–S(1) 63.18(10), O(3)–C(7)–C(9) 111.85(14), O(3)–C(7)–C(1) 111.78(13), C(9)–C(7)–C(1) 118.78(14), C(5)–C(7)–C(1) 86.11(13), C(6)–C(8)–S(1) 61.87(10).

Let us discuss the possible pathways for the formation of compounds **3** and **4**. Each of the dihalides **2a**,**b** has two reaction centres, namely, a benzyl bromide moiety and an α-halosulfone moiety. Both of these centres are sensitive to the action of bases and/or nucleophiles. Boiling of compounds **2a**,**b** in a water–dioxane solution of NaOH results in their transformation involving both reaction centres. However, the fact that dibromide **2a** is transformed into alcohol **5** under milder conditions indicates that the nucleophilic substitution of benzylic bromine is a faster process. Thus, compounds **3** and **4** are formed from alcohol **5**, which was confirmed by a direct experiment.

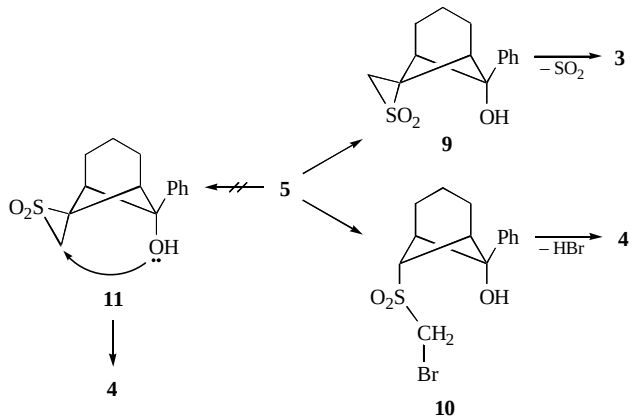
The transformation of alcohol **5** into methylenic derivative **3** is believed to result from the Ramberg–Bäcklund reaction[8] and occurs in a tandem process of 1,3-dehydrobromination to give episulfone **9** followed by its desulfonation. Although attempts at detecting episulfone **9** during the treatment of alcohol **5** with a base failed, it may be assumed that the stereochemistry of alcohol **5** 1,3-dehydrobromination is the same as that of ether **6**. Furthermore, literature precedents[8,9] suggest that α-bromosulfones **5** and **6** should indeed undergo stereoselective dehydrobromination to give episulfones **9** and **8**, respectively, since it has been found that elimination obeys the W-stereochemistry[10] and the α-proton is abstracted from a conformation of the starting bromosulfone in which it is flanked by oxygen atoms of the sulfo group. Thus, alcohol **3** is formed due to fragmentation of episulfone **9** and is a 'normal' product of the Ramberg–Bäcklund reaction (Scheme 3).

¶ *X-Ray diffraction data*: crystals of $C_{15}H_{18}O_3S$ **8** are monoclinic, space group *P*21/*c*, $T = 293(2)$ K, $a = 8.451(4)$ Å, $b = 16.633(6)$ Å, $c = 10.703(5)$ Å, $\beta = 110.55(3)°$, $V = 1409(1)$ Å^3, crystal size 0.50×0.20×0.20 mm, $Z = 4$, $d_{calc} = 1.312$ g cm^{-3}, $F(000) = 592$, graphite monochromator, MoKα irradiation, $\lambda = 0.71073$ Å, $\mu = 0.231$ mm^{-1}. The intensities of 3292 reflections (3090 independent ones, $R_{int} = 0.0273$) were measured using a Siemens P3/PC diffractometer (θ–2θ scanning, $2\vartheta_{max} = 54°$). The structure was solved by a direct method using the SHELXTL PLUS 5.0 program package.[13] The positions of the hydrogen atoms were revealed by difference synthesis of the electron density. Refinement of F^2 over 244 parameters in an anisotropic approximation (isotropic for H atoms) by the full-matrix least squares method for 2756 reflections was carried out to $R_1 = 0.0455$ [for 2171 reflections with $F > 4\sigma(F)$], $wR_2 = 0.1213$, $S = 1.064$. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Communications*, 1998, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/24.



Scheme 2 *Reagents and conditions*: i, NaOH in aqueous dioxane; ii, Na_2CO_3 in aqueous THF; iii, MeONa in MeOH; iv, Bu^{t}OK in THF.

In our opinion, the transformation of alcohol **5** to oxatricyclic sulfone **4** does not involve a 1,3-elimination step but results from base-catalysed epimerisation at the C(6) atom followed by 1,6-elimination in the intermediate compound **10**. This assumption agrees with the fact established in the literature[11] that deuteroexchange and epimerisation at the α-C atom in a halosulfone occur much faster than the formation of an episulfone. An *a priori* possible alternative pathway for the formation of product **4** by intramolecular nucleophilic ring opening at the C–C bond in episulfone requires this episulfone (in the case we are studying, episulfone **9**) to have a configuration at C(6) different from that in compound **9**. We rule this pathway out for the reason that, as noted above, the formation of such intermediates during the transformations seems unlikely.



Scheme 3

Taking Scheme 3 into account, the fact that chlorobromide **2b** is mainly transformed into sulfone **4** on treatment with a water–dioxane solution of NaOH should be interpreted as an indication that in the transition from bromide **2a** to chloride **2b**, competition between intramolecular C- and O-alkylation tends to favour the latter reaction. As the chloromethyl fragment is a 'harder' electrophilic centre than the bromomethyl fragment, the observed result finds an explanation within the scope of the HSAB concept.[12] This result is also consistent with data on the analogous formation of 1-oxa-3-thiacyclopent-4-ene 3,3-dioxides from α-halomethylsulfonylketones observed by Block *et al.*[1]

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