Transannular Ring Expansion in the Acid-Catalyzed Reaction of the Oxirane Derived from Spirocyclopropane-Substituted Bicyclo[2.2.2]oct-2-ene

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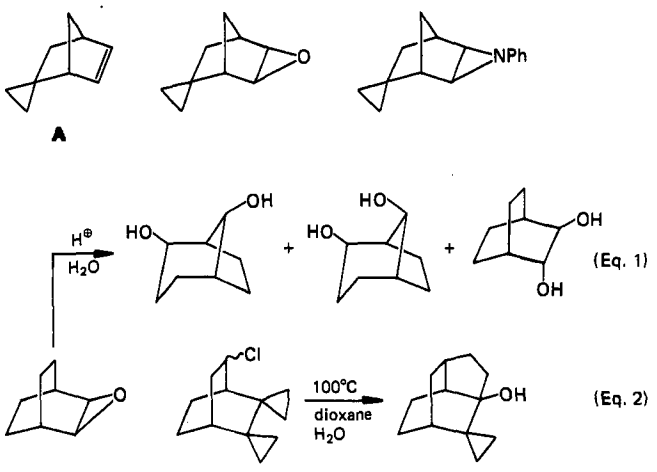
Spiro[bicyclo[2.2.2]oct-5-ene-2,1′-cyclopropane] (**1**), obtained by [4 + 2] cycloaddition of 1,3-cyclohexadiene to methylenecyclopropane, was epoxidized to give the *exo* and *endo* epoxides **2**. The *exo* epoxide **2** gave with trifluoroacetic acid the 7,9-disubstituted homobrendane **7b** (main product) and the 2,6-disubstituted isotwistane **7a** (minor product) via transannular ring expansion of the spirocyclopropane substituent with and without skeletal rearrangement of the bicyclic ring system, respectively. No 1,2-*trans* adducts were observed, as is the case in the reaction of the spiroalkene **1** with arenesulfenyl chloride, which in turn gave no ring-expanded products. The fact that an isomeric mixture of all four possible 1,2-*trans* adducts **4** were obtained, proves that the spirocyclopropane substituent promotes neither regio- nor stereoselectivity. In contrast, bicyclo[2.2.2]oct-2-en-5-one proceeded with arenesulfenyl chloride regio- and stereoselectively, leading to (*exo*-5,*endo*-6)-6-chloro-5-(*p*-tolylthio)bicyclo[2.2.2]octan-2-one (**5a**). The stereochemistry of the latter was established by means of X-ray analysis of its sulfoxide derivative **6a**.

Transannulare Ringerweiterung in der säurekatalysierten Reaktion des Oxirans aus dem spirocyclopropansubstituierten Bicyclo[2.2.2]oct-2-en

Das durch [4 + 2]-Cycloaddition aus Methylencyclopropan und 1,3-Cyclohexadien zugängliche Spiro[bicyclo[2.2.2]oct-5-en-2,1′-cyclopropan] (**1**) wurde zu den *exo*- und *endo*-Epoxiden **2** epoxidiert. Das *exo*-Epoxid **2** reagierte mit Trifluoressigsäure unter transannularer Ringerweiterung des Spirocyclopropansubstituenten mit (oder ohne) Gerüstumlagerung des bicyclischen Systems zu dem 7,9-disubstituierten Homobrendan **7b** (Hauptprodukt) und zu dem 2,6-disubstituierten Isotwistan **7a** (Nebenprodukt). 1,2-*trans*-Additionsprodukte wurden nicht nachgewiesen, im Gegensatz zur Reaktion von **1** mit Arensulfenylchlorid, in der aber keine Umlagerungsprodukte beobachtet wurden. Das Isomerengemisch der vier gebildeten 1,2-*trans*-Additionsprodukte bewies den fehlenden Einfluß des Spirocyclopropansubstituenten auf die Regio- und Stereoselektivität, die im Fall des Bicyclo[2.2.2]oct-2-en-5-on mit Arensulfenylchlorid nachgewiesen werden konnte. Das Hauptprodukt war (*exo*-5,*endo*-6)-6-Chlor-5-(*p*-tolylthio)-bicyclo[2.2.2]octan-2-on (**5a**), dessen Stereochemie über das entsprechende Sulfoxid **6a** mittels Röntgenstrukturanalyse ermittelt wurde.

In a previous paper[1] we have shown that spirocyclopropane-substituted norbornanes on treatment with electrophiles readily undergo transannular ring expansion of the spirocyclopropane moiety leading to functionalized brendanes with and without skeletal rearrangement. In comparison to the spiro[cyclopropane-norbornene] **A**, preliminary experiments of the corresponding spiro[cyclopropane-bicyclo[2.2.2]octene] (**1**) with arenesulfenyl chloride gave exclusively an addition product (cf. Results), with no signs of transannular participation of the remote spirocyclopropane ring. Indeed, it has been reported[2] that the bicyclo[2.2.2]oct-2-ene oxide proved less prone to skeletal rearrangement (Eq. 1), since appreciable amounts (15%) of the addition product bicyclo[2.2.2]octane-2,3-diol was formed on acid treatment.

However, in view of the fact that the bicyclo[3.2.1]octanediols (skeletal rearrangement) were the major products (64%), it was of interest to see whether the spirocyclopropane-substituted bicyclo[2.2.2]oct-2-ene oxide **2** would exhibit transannular ring expansion of the spirocyclopropane group. Herewith a potentially useful synthetic entry into functionalized homobrendanes and isotwistanes might be made available. In fact, the only precedent, to the best of our knowledge, constitutes the hydrolysis reaction in Eq. 2, affording the isotwistane under transannular ring expansion of the remote spirocyclopropane substituent[3]. Presently we report our experiences with the oxirane **2** derived from the spirocyclopropane-substituted bicyclo[2.2.2]oct-2-ene **1**.



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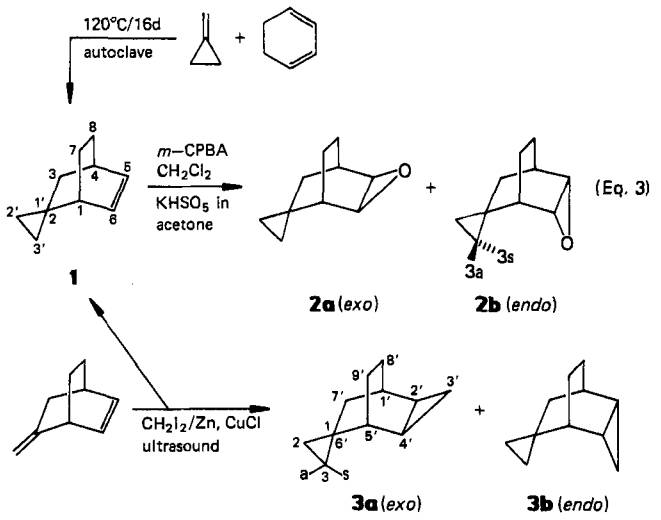
Results: A) Starting Materials

In the synthetic scheme of Eq. 3 the preparation of the spirobicyclooctene **1** and its oxides **2** is presented. Cycloaddition of methylenecyclopropane and 1,3-cyclohexadiene under pressure afforded **1** in ca. 50% yield, which was obtained analytically pure by means of preparative GC. Also some minor cycloaddition products, presumably [2 + 2] adducts, were formed but were not further purified and characterized. Nevertheless, the cycloaddition route in Eq. 3 was considerably more fruitful than methylenation of 5-methylenebicyclo[2.2.2]oct-2-ene under Simmons-Smith conditions[4]. Mixtures of the desired spirobicycloalkene **1** and the cyclopropanated derivatives **3a, b** were obtained, which were difficult to separate for preparative purposes. Under exhaustive methylenation conditions only the *exo,endo* products **3** were formed.



Epoxidation of the spirobicycloalkene **1** with *m*-chloroperbenzoic acid (*m*-CPBA) or with potassium caroate in acetone[5] afforded a mixture of *exo,endo* epoxides **2** (Eq. 3). Of these two methods, *m*-CPBA gave the higher yield (77%), but the dioxirane (formed from acetone and potassium caroate[5]) led to a higher proportion (74:26) of the desired *exo*-**2** isomer. Flash chromatography enabled separating the mixture of *exo,endo* epoxides **2** into its pure isomers.

B) Structural Assignment of Starting Materials

In the case of the spirobicycloalkene **1**, the ^{13}C-NMR spectrum was definitive in the elucidation of its structure. The bridgehead carbon signals appear as doublets at δ = 31.42 (C-4) and δ = 40.12 (C-1). The down-field resonance is assigned to C-1 due to deshielding by the spirocyclopropane substituent[6]. A similar down-field shift is also experienced by the methylenic triplet of C-3 at δ = 39.51, compared to the methylenic triplets of the ethano bridge (C-7,8) at δ = 24.73 and 25.24. The ^{1}H-NMR spectrum corroborates this assignment, in that the proton of the bridgehead proton multiplets at δ = 1.8–1.9 (1-H) is shifted to higher field by the spirocyclopropane group[6] than the bridgehead multiplet at δ = 2.4–2.6 (4-H).

For the *exo,endo* epoxides **2** the spirocyclopropane moiety caused also the expected[6] low-field shifts of the C-1′ versus C-5′ carbons, i.e. in the *exo* isomer these doublet carbon signals are located at δ = 29.68 (C-1′) and δ = 38.46 (C-5′) and in the *endo* isomer at δ = 28.70 (C-1′) and 38.56 (C-5′). Of the corresponding bridgehead protons 1′-H and 5′-H, only the signal of the former could be assigned in the 400-MHz ^{1}H-NMR spectra, located at δ = 2.17 (m_c) for both isomers. The 5′-H bridgehead resonances overlap with the methylenic 7′-H, 8′-H, and 9′-H signals due to the up-field shift by the spirocyclopropane group.

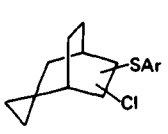
The assignment of the *exo,endo* stereochemistry rests mainly on the effects caused by adding Eu(fod)$_3$ as shift reagent[7] in the ^{13}C-NMR spectra (cf. Experimental). Addition of Eu(fod)$_3$ to the *exo* isomer **2a** expectedly shifted the C-8′ and C-9′ carbons down-field by $\Delta\delta$ = 2.14 and 2.03 ppm, respectively, while for the *endo* isomer **2b** the shifts amounted to only $\Delta\delta$ = 0.36 ppm for both the C-8′ and C-9′ carbons. Furthermore, the bridgehead carbon signals of C-1′ and C-5′ were shifted to lower field for both isomers, but for the *exo* isomer **2a** to a greater extent, i.e. $\Delta\delta$ = 2.16 (C-1′) and $\Delta\delta$ = 1.70 (C-5′), than for **2b**, i.e. $\Delta\delta$ = 1.18 (C-1′) and $\Delta\delta$ = 1.12 (C-5′). Steric repulsion by the spirocyclopropane substituent in **2b** is presumably responsible for this differentiation (cf. Dreiding models), allowing better complexation of the Eu(fod)$_3$ in the case of the *exo* isomer. The greater down-field shift of the C-7′ methylene group in **2b** compared to **2a**, i.e., $\Delta\delta$ = 1.47 versus $\Delta\delta$ = 0.79, is consistent with this assignment.

Confirmative help was also derived from the ^{1}H-NMR spectra, although these were exceedingly complex due to extensive overlap of the resonances. Nevertheless, while the signals of the epoxy protons 2′-H and 4′-H appeared as a centered multiplet at δ = 3.21 for the *endo* isomer **2b** (the spirocyclopropane ring is too far away for significant anisotropic effects), for the *exo* isomer **2a** these were differentiated as ddd patterns at δ = 3.29 (4′-H) and δ = 3.33 (2′-H). In addition to the vicinal couplings ($J_{2',4'} = J_{4',5'} = J_{1',2'}$ = 4.5 Hz) also the W-couplings ($J_{4',9a'} = J_{2',8a'}$ = 0.75 Hz) could be observed, giving rise to the ddd patterns. Finally, in **2b** the spirocyclopropyl 3a-H signal appears as a significantly up-field shifted centered multiplet at δ = 0.09 due to anisotropic effects of the *endo* epoxide ring. The remaining three spirocyclopropyl signals bunch together at δ = 0.23–0.52 (m), analogous to the four spirocyclopropyl resonances of the *exo* isomer **2a** at δ = 0.25–0.50 (m).

C) Transformations

As already stated, the electrophilic addition of *p*-toluenesulfenyl chloride (ArSCl) to the spirobicycloalkene **1** gave only the addition products **4**. By means of ^{1}H- and ^{13}C-NMR analysis (electronic integration against an external standard) of the crude reaction mixture prior to workup, it could be shown that the spirocyclopropane moiety had remained intact. The characteristic[1] arenesulfenyl-substituted carbon signals occurred as a set of four doublets at δ = 57.27, 57.89, 58.65, and 59.47 and those of the characteristic[1] chlorine-

substituted carbons as a set of four doublets at δ = 64.81, 65.19, 66.25, and 67.05, both in approximate ratios of 1:5:7:12, indicating that all four possible isomers of the *trans* addition products **4** had been formed. It was not possible to separate these by means of capillary GC, so that merely the mixture was characterized, without elucidation of the stereochemistry of the individual isomers.



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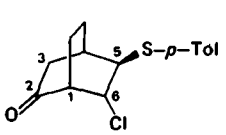
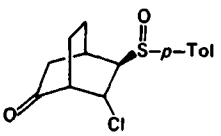


5a



6a

In contrast to the complete lack of regioselectivity of the spirobicycloalkene **1** towards *p*-toluenesulfenyl chloride, bicyclo[2.2.2]oct-2-en-5-one gave **5a** as major product[8]. The crude product mixture contained both regio isomers **5a,b** in 62:38 ratio, from which isomer **5a** was isolated by centrifugal chromatography. Oxidation of the mixture of **5a,b** with *m*-CPBA afforded the sulfoxide **6a,b** in 35% yield, from which the main isomer **6a** was isolated in pure form. Its structure was rigorously established by means of X-ray analysis (Figure 1, Tables 1 and 2).

Table 1. Atomic coordinates [× 10^4] and isotropic thermal parameters [pm^2 × 10^{-1}]

	x	y	z	U
S	2470(1)	530(2)	5456(2)	56(1)*
Cl	2604(1)	-901(2)	10712(2)	80(1)*
O	2406(2)	1841(4)	4653(5)	82(2)*
C(1)	1306(3)	-1096(5)	8880(7)	56(2)*
C(2)	1031(3)	-132(5)	10187(7)	53(2)*
O(2)	734(2)	-435(4)	11568(5)	81(2)*
C(3)	1127(3)	1227(5)	9570(7)	57(2)*
C(4)	1381(3)	1226(5)	7598(7)	53(2)*
C(5)	2116(2)	594(5)	7769(6)	45(2)*
C(6)	2080(3)	-740(5)	8572(7)	52(2)*
C(7)	879(3)	-956(6)	7018(8)	74(2)*
C(8)	885(3)	447(6)	6337(7)	66(2)*
C(9)	3380(2)	328(5)	6301(6)	48(2)*
C(10)	3663(3)	-900(5)	6380(7)	53(2)*
C(11)	4369(3)	-1029(5)	6914(7)	53(2)*
C(12)	4786(3)	33(5)	7325(6)	49(2)*
C(13)	4480(3)	1258(6)	7247(7)	55(2)*
C(14)	3773(3)	1409(5)	6727(7)	53(2)*
C(15)	5563(3)	-137(7)	7890(7)	71(2)*

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths [pm] and bond angles [°] of **6a**. The standard deviations are given in parentheses

S-O	147.4(4)	S-C(5)	184.1(5)
S-C(9)	181.2(5)	Cl-C(6)	177.1(5)
C(1)-C(2)	149.2(8)	C(1)-C(6)	156.2(7)
C(1)-C(7)	151.4(8)	C(2)-O(2)	122.2(6)
C(2)-C(3)	148.9(8)	C(3)-C(4)	153.1(7)
C(4)-C(5)	154.9(7)	C(4)-C(8)	149.4(7)
C(5)-C(6)	149.9(7)	C(7)-C(8)	153.2(9)
C(9)-C(10)	138.1(8)	C(9)-C(14)	136.9(7)
C(10)-C(11)	138.3(7)	C(11)-C(12)	137.7(7)
C(12)-C(13)	139.5(8)	C(12)-C(15)	152.2(7)
C(13)-C(14)	138.6(7)		

O-S-C(5)	107.1(2)	O-S-C(9)	106.5(2)
C(5)-S-C(9)	96.8(2)	C(2)-C(1)-C(6)	108.5(4)
C(2)-C(1)-C(7)	107.2(4)	C(6)-C(1)-C(7)	107.8(4)
C(1)-C(2)-O(2)	123.2(5)	C(1)-C(2)-C(3)	112.7(4)
O(2)-C(2)-C(3)	124.0(5)	C(2)-C(3)-C(4)	109.2(4)
C(3)-C(4)-C(5)	106.5(4)	C(3)-C(4)-C(8)	108.8(4)
C(5)-C(4)-C(8)	110.6(4)	S-C(5)-C(4)	110.1(3)
S-C(5)-C(6)	110.2(3)	C(4)-C(5)-C(6)	110.3(4)
Cl-C(6)-C(1)	109.6(3)	Cl-C(6)-C(5)	112.2(3)
C(1)-C(6)-C(5)	110.2(4)	C(1)-C(7)-C(8)	110.7(5)
C(4)-C(8)-C(7)	109.8(4)	S-C(9)-C(10)	119.0(4)
S-C(9)-C(14)	118.5(4)	C(10)-C(9)-C(14)	122.3(4)
C(9)-C(10)-C(11)	118.2(5)	C(10)-C(11)-C(12)	121.4(5)
C(11)-C(12)-C(13)	118.8(5)	C(11)-C(12)-C(15)	120.2(5)
C(13)-C(12)-C(15)	121.0(5)	C(12)-C(13)-C(14)	120.8(5)
C(9)-C(14)-C(13)	118.5(5)		

The transformation scheme of Eq. 4 reveals that the *exo* epoxide **2a** underwent transannular ring expansion of the spirocyclopropane substituent leading to the hydroxy esters **7a** (isotwistane) and **7b** (homobrendane) in 80% yield (**7a**/**7b** ratio 35:65 by capillary GC). By means of flash chromatography 16% of pure **7a** and 46% of pure **7b** was obtained for further characterization. Saponification of the individual hydroxy esters with KOH in aqueous ethanol led to the diols **8a** (94%) and **8b** (31%). X-ray analysis, unfortunately of poor quality (R = 0.28), is consistent with the

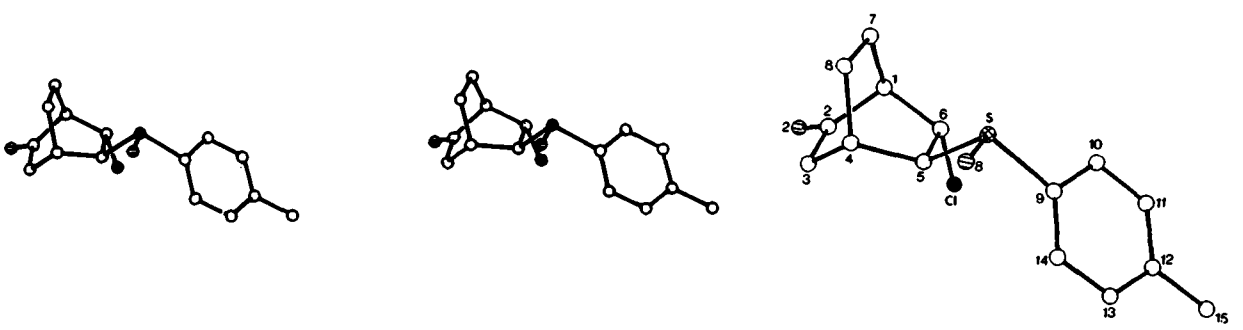
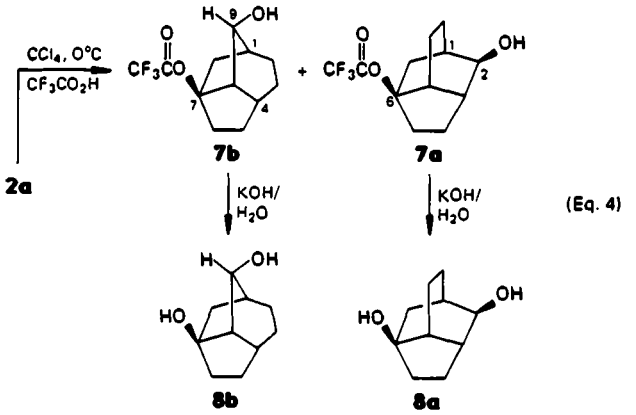


Figure 1. Perspective drawing and stereopair of the crystal structure of the chloro sulfoxide **6a**; the numbering of the atoms corresponds to Tables 1 and 2; open circles are carbons, hatched circles oxygens, the checkered circle sulfur, and the solid circle chlorine

connectivity of the atoms proposed for the structure of the dihydroxyisotwistane **8a**.



(Eq. 4)

The *endo* epoxide **2b** gave on treatment with trifluoroacetic acid a complex mixture of products (at least six by capillary GC) which could not be separated by preparative chromatographic methods. By means of coinjection of authentic substances, minor amounts of products with retention times corresponding to the hydroxy esters **7a,b** could be detected.

D) Structural Assignment of Isotwistanes and Homobrendanes

The ^{1}H- and ^{13}C-NMR spectra of the isotwistanes **7a** and **8a** and of the homobrendanes **7b** and **8b** were complex due to extensive signal overlap, making a rigorous assignment of all the resonances difficult. Although of poor quality, as already stated, an X-ray structure of the 2,6-dihydroxyisotwistane **8a** was available, which was helpful in the spectroscopic elucidation.

Table 3. Characteristic ^{1}H- and ^{13}C-NMR data of the disubstituted isotwistanes and homobrendanes[a]

No.	2-H (pseudo-t)	C-2 (d)	C-6 (s)
7a	4.30 ($J_{2,1} = J_{2,3} = 5.0$ Hz)	71.78	96.90
8a[b]	4.16 ($J_{2,1} = J_{2,3} = 4.5$ Hz)	71.21	83.37
No.	**9-H (pseudo-t)**	**C-7 (s)**	**C-9 (d)**
7b	3.58 ($J_{9,1} = J_{9,8} = 3.8$ Hz)	89.47	76.65
8b[c]	3.54 ($J_{9,1} = J_{9,8} = 4.2$ Hz)	77.23 (75.73)	75.58 (75.98)

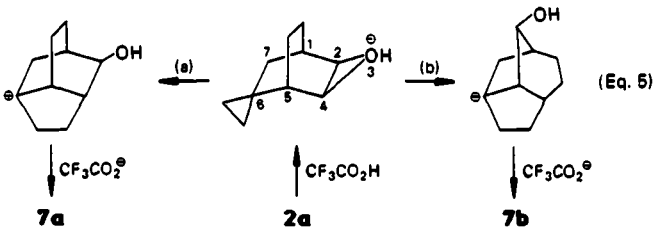
[a] Unless otherwise stated, proton resonances were measured at 400 MHz and carbon resonances at 100 MHz in $CDCl_3$, using the latter also as internal standard; all chemical shifts (δ values) pertain to the pure isomers; for numbering of the atoms cf. Eq. 4. – [b] Run in [D_6]DMSO with DMSO as internal standard; the hydroxy proton signals appeared at δ = 4.46 (6-OH) and δ = 4.67 (2-OH; $J_{2,OH}$ = 3.6 Hz), exchangeable with D_2O. – [c] Carbon resonances in parentheses refer to [D_6]DMSO as solvent.

The few interpretable proton and carbon resonances characteristic of these complex structures are summarized in Table 3. These are the 2-H signals of the 2,6-disubstituted isotwistane series **7a** and **8a** and the 9-H protons of the 7,9-disubstituted homobrendane series **7b** and **8b**, appearing as pseudo triplets due to vicinal coupling by the 1-H and 3-H and by the 1-H and 8-H protons, respectively. For additional confirmation, the known 2-hydroxyisotwistane is being cited[9], which has its 2-H proton resonance at δ = 3.42 (60 MHz, $CDCl_3$).

The characteristic carbon resonances (Table 3) pertain to the disubstituted carbons in these substances, i.e. the doublet carbons C-2 for the isotwistanes **7a** and **8a** and C-9 for the homobrendanes **7b** and **8b** and the singlet carbons C-6 and C-7, respectively. The remaining carbon resonances are in accord with those reported for twistane[10] and homobrendane[11].

Discussion

Surprising was the finding that the spirobicycloalkene **1** gave on treatment with *p*-toluenesulfenyl chloride (ArSCl) only *trans*-1,2 addition, leading to all possible regio- and stereoisomers **4**. In contrast, the corresponding spironorbornene gave with ArSCl mainly transannular ring expansion products (with and without skeletal rearrangement), while the 1,2-addition (minor product) proceeded regioselectively[1]. We confirmed that arenesulfenyl chloride addition to bicyclo[2.2.2]oct-2-en-5-one takes place regioselectively[8], affording the adduct **5a**, whose structure was unequivocally established by means of X-ray analysis (Figure 1) of its sulfoxide derivative **6a**. Consequently, until the regio- and stereochemistry of the isomeric adducts **4** derived from the spirobicycloalkene is established, it is not possible to rationalize the directing effect of the remote spirocyclopropane moiety in the bicyclo[2.2.2]oct-2-ene **1** substrate. Nevertheless, the present data clearly reveal that in the electrophilic addition of arenesulfenyl chlorides, the spirocyclopropane-substituted bicyclo[2.2.2]oct-2-ene **1** is much less prone to transannular ring expansion (with and without skeletal rearrangement) of the remote spirocyclopropane group than the corresponding norbornene system[1]. The intermediary episulfonium ion derived from **1** is trapped more efficiently by the chloride ion prior to transannular ring expansion or skeletal rearrangement.



(Eq. 5)

Fortunately, the protonated *exo* oxirane **2a** is much more active towards transannular ring expansion of the remote spirocyclopropane moiety. As shown in the mechanistic scheme of Eq. 5, first ring expansion (path a) followed by nucleophilic trapping, leads to the isotwistane derivative **7a**

as minor product. On the other hand, first skeletal rearrangement of the antiperiplanar C-5/C-6 σ-bond and subsequent ring expansion (path b) followed by nucleophilic trapping, generates the homobrendane derivative **7b** as major product.

In this context it is significant to mention that the *endo*-**2** epoxide gave on treatment with trifluoroacetic acid a complex mixture of products which contained only minor amounts of the transannular ring expansion products. Clearly, the remote spirocyclopropane unit must be antiperiplanar to the protonated epoxide ring for optimal transannular ring expansion. With this provision, functionalized complex tricyclic carbon skeletons such as the isotwistanes and the homobrendanes can be prepared directly from readily available spirocyclopropane-substituted bicyclo[2.2.2]-oct-2-enes.

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Experimental

General Aspects: Boiling and melting points are uncorrected, the latter were taken on a Reichert Thermovar Kofler apparatus. – Infrared (IR) spectra were obtained on a Beckman Acculab 4. – ^{1}H-NMR spectra were run either on an Hitachi-Perkin-Elmer R 24 B (60 MHz), Varian EM 390 (90 MHz) or Bruker WM 400 (400 MHz), using TMS as internal standard, and ^{13}C-NMR spectra either on a Bruker WH 90 (22.64 MHz) or on a Bruker WM 400 (100.6 MHz), using $CDCl_3$ as internal standard. The chemical shifts are reported in δ values. – Mass spectra (MS) were measured either on a Varian MAT CH 7 or on a Finnigan MAT 44, coupled with GC. – Combustion analyses for elemental composition were either obtained in-house or from Prof. G. Maier's staff at the Institute of Organic Chemistry (Gießen). – Thin-layer chromatography (TLC) was run on Polygram SIL/G/UV (40 × 80 mm) from Macherey, Nagel & Co. Column chromatography utilized silica gel (70–230 mesh ASTM, activity III), using an adsorbent to substrate ratio of at least 20:1. – Analytical gas chromatography was performed on a Carlo Erba Strumentazione Model 2900, Fractovap Series, or on Model 4100 instruments, equipped with capillary columns and FID. – Preparative gas chromatography employed a Carlo Erba Strumentazione Model 4200.

Commercial reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Known compounds were prepared according to literature procedures and purified accordingly. Cycloadditions under pressure were run in an 80-ml steel autoclave, Carl Roth GmbH, Karlsruhe (FRG). Unless otherwise stated, stirring was performed magnetically, room temp. was ca. 20°C, drying after aqueous workup was carried out with anhydrous $MgSO_4$ or Na_2SO_4, and roto-evaporation was performed at aspirator pressure (15–20 Torr at room temp.).

X-ray Crystallography of the Sulfoxide **6a**: The orientation matrix and the cell parameters were determined from a clear colorless crystal of dimensions 0.2 × 0.8 × 0.15 mm on a Syntex-P3 four-circle diffractometer. Measurement of intensities: ω scan, 1° range, Mo-K_α, $2\Theta \leq 55°$. The intensities of 3036 reflections were measured, of which 2178 reflections with $F > 3\sigma(F)$ were applied for the structure determination. The structure was solved by direct phase determination. From the resulting *E*-map approximate positions of all non-hydrogen atoms could be refined by anisotropic least-squares cycles to $R = 0.085$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in further refinements. The sulfoxide **6a** crystallizes in the space group $P2_1/a$ with $a = 1917.2(8)$, $b = 1034.5(8)$, $c = 716.2(4)$, and $\beta = 94.65(4)°$, $Z = 4$, $d_x = 1.392$ g·cm^{-3}. All atomic parameters are listed in Table 1 and the labeling of the atoms is given in Figure 1. Bond distances and angles are summarized in Table 2.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-52188, the names of the authors, and the journal citation.

Spiro[bicyclo[2.2.2]oct-5-ene-2,1'-cyclopropane] (**1**): 360 mg (4.50 mmol) of 1,3-cyclohexadiene, 243 mg (4.50 mmol) of methylenecyclopropane, and ca. 5 mg of hydroquinone were allowed to react at 120°C in an 80-ml steel autoclave. Monitoring the reaction progress by 60-MHz ^{1}H NMR showed after 16 d 50% conversion to the spirocyclopropane **1**. The latter was purified by means of kugelrohr distillation, affording 300 mg (50%) of a colorless liquid, b.p. 80–83°C/18 Torr. An analytical sample was obtained by preparative gas chromatography, employing a 6-m × 7-mm glass column [packed with 10% SE-30 on Chromosorb W and operated at column, detector, and injector temp. of 100, 180, and 180°C, respectively, and a carrier gas pressure (N_2) of 0.6 kg/cm^2]. – IR (CCl_4): 3060 cm^{-1}, 3040, 2990, 2950, 2860, 1600, 1450, 1435, 1410, 1355, 1000, 899, 705, 675. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.1–0.5 (m; 4H, cyclopropyl-H), 1.2–1.7 (m; 6H, 3-H, 7-H, 8-H), 1.8–1.9 (m; 1H, 1-H), 2.4–2.6 (m; 1H, 4-H), 6.31 (ddd, $J_{6,5} = 8$ Hz, $J_{6,1} = 6.5$ Hz, $J_{6,4} = 2.0$ Hz; 1H, 6-H), 6.36 (ddd, $J_{5,6} = 8$ Hz, $J_{5,4} = 6.5$ Hz, $J_{5,1} = 2.0$ Hz; 1H, 5-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 12.50 and 15.94 (two t; C-2', C-3'), 21.06 (s; C-1'), 24.73 and 25.24 (two t; C-7, C-8), 31.42 (d; C-4), 39.51 (t; C-3), 40.12 (d; C-1), 134.13 (d; C-5), 134.64 (d; C-6). – MS (70 eV): *m/z* (%) = 134 (17; M^+), 92 (29), 91 (61), 80 (100; $C_6H_6^+$), 78 (45), 77 (21), 41 (9).

$C_{10}H_{14}$ (134.2) Calcd. C 89.49 H 10.51
Found C 89.46 H 10.49

Cyclopropanation of 5-Methylenebicyclo[2.2.2]oct-2-ene: 11.5 g of zinc (coarse grains) was vigorously stirred mechanically in 150 ml of dimethoxyethane in an ultrasound bath at room temp. for 30 min, and while stirring was added subsequently 17.2 g (175 mmol) of Cu(I) chloride. After stirring for another 30 min at room temp. and another 30 min at 60°C, to this heterogeneous mixture was added dropwise 5.30 g (43.8 mmol) of methylenebicyclooctene and 46.9 g (175 mmol) of diiodomethane. The resulting greyish brown reaction mixture was refluxed for 12 h. After cooling to room temp. was added 200 ml of a saturated aqueous NH_4Cl solution. The organic phase was separated and extracted with 3:1 petroleum ether (30–50 C)/ether (2 × 100 ml). The combined organic phases were washed with saturated aqueous NaCl solution (2 × 100 ml), dried, and the solvent was roto-evaporated leading to 3.20 g (54%) of a yellow oil. Kugelrohr distillation at 100–120°C/14 Torr afforded 750 mg (23%) of the isomeric spirotricyclononanes **3a,b** in 1:2 proportion (by capillary GC), respectively, as colorless oil. By means of preparative GC on a 1.5-m × 8-mm glass column [packed with 10% Apiezon on Chromosorb WHP and operated at column, detector, and injector temp. of 130, 180, and 170°C, respectively, and a carrier gas pressure (N_2) of 0.6 kg/cm^2] the isomers could be separated. – IR (CCl_4) of the isomers **3a,b**: 3070 cm^{-1}, 3005, 2940, 2905, 2860, 1455, 1100, 1030, 1005, 940. – MS (70 eV) of the isomers **3a,b**: *m/z* (%) = 148 (6; M^+), 134 (2;

$C_{10}H_{14}^+$), 133 (19), 120 (19; $C_9H_{12}^+$), 119 (34), 105 (44), 91 (82), 79 (100; $C_6H_7^+$), 77 (35), 41 (31).

(1'α,2'α,4'α,5'α)-Spiro[cyclopropane-1,6'-tricyclo[3.2.2.0^{2,4}]-nonane] (**3a**): ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 0.3–0.4 (m; 4H, cyclopropyl-H), 0.45–0.48 (m; 1H, 3'-H), 0.63 (m_c; 1H, 3'-H), 0.84 (m_c; 1H), 0.94 (m_c; 1H), 1.10 (m_c; 1H), 1.2–1.4 (m; 2H), 1.4–1.6 (m; 3H), 1.6–1.7 (m; 1H), 1.99 (m_c; 1H, 1'-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 4.70 (t; C-3'), 13.25 and 13.63 (two d; C-2', C-4'), 14.19 and 15.27 (two t; C-2, C-3), 20.46 (s; C-6'), 23.31 and 23.83 (two t; C-8', C-9'), 26.55 (d; C-1'), 35.29 (d; C-5'), 39.57 (t; C-7').

(1'α,2'β,4'β,5'α)-Spiro[cyclopropane-1,6'-tricyclo[3.2.2.0^{2,4}]-nonane] (**3b**): ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 0.04–0.14 (m; 1H, cyclopropyl-H), 0.18–0.34 (m; 3H, cyclopropyl-H), 0.4–0.5 (m; 1H, 3'-H), 0.8–0.9 (m; 3H, 2'-H, 4'-H, 3'-H), 0.92 (m_c; 1H), 1.34 (m; 2H), 1.4–1.7 (m; 4H), 1.76 (m_c; 1H, 1'-H). – ^{13}C NMR ($CDCl_3$; 100.6 MHz): δ = 3.29 (t; C-3'), 12.54 and 13.27 (two d; C-2', C-4'), 14.30 and 16.58 (two t; C-2, C-3), 18.28 (s; C-6'), 25.10 and 25.95 (two t; C-8', C-9'), 26.25 (d; C-1'), 35.87 (d; C-5'), 36.78 (t; C-7').

Epoxidation of the Spiroalkene **1**. – A) *Caroate-Acetone:* While stirring mechanically, to a mixture of 400 mg (2.98 mmol) of the spiroolefin **1** in 50 ml of CH_2Cl_2, 20 ml of H_2O and 4 ml of acetone was added within ca. 2 h 396 mg (1.50 mmol) of [18]-crown-6 and ca. 5 mg of (EDTA)Na_2, followed by a solution of 2.27 g (14.9 mmol) of $KHSO_5$ in 40 ml of H_2O, controlling the pH of the mixture at ca. 7.5–8.0 and the temp. below 8°C by means of an ice bath. After 24 h at room temp., the organic phase was separated, the aqueous phase extracted with CH_2Cl_2 (2 × 50 ml), the combined organic phases were dried, and the solvent was roto-evaporated. Kugelrohr distillation at 60–70°C/0.1 Torr gave 80 mg (18%) of a waxy, colorless oil of the isomeric oxiranes **2a,b** (**2a**/**2b** = 74:26) as determined by capillary GC, using a 50-m glass column (Carbowax 20 M), operated at injector, detector, and column temp. of 190, 200, and 90°C, respectively, and a carrier gas pressure (N_2) of 0.3 kg/cm^2.

B) *m-Chloroperbenzoic Acid:* 2.00 g (14.9 mmol) of the spiroolefin **1** in 50 ml of CCl_4 was treated with 3.60 g (20.9 mmol) *m*-chloroperbenzoic acid (*m*-CPBA) at 0°C in the presence of ca. 100 mg of solid $NaHCO_3$. After stirring for 48 h at room temp. the solid material was removed by filtration and the filtrate washed with saturated aqueous Na_2SO_3 (2 × 50 ml), followed by saturated aqueous $NaHCO_3$ (2 × 50 ml). After drying and roto-evaporation of the solvent, 1.73 g (77%) of the oxiranes **2a,b** was obtained as yellow oil. Capillary GC as under method A) gave a **2a**:**2b** ratio of 62:38. Flash chromatography on silica gel (adsorbent/substrate of 50:1), eluting with a 12:1 mixture of petroleum ether (30–50°C) and ethyl acetate, allowed separation of the mixture into the pure isomers **2a** and **2b**. – IR (CCl_4) of the mixture **2a,b**: 3070 cm^{-1}, 3000, 2940, 2860, 1460, 1410, 1135, 1010, 950, 850, 650. – MS (70 eV) of the mixture **2a,b**: *m/z* (%) = 150 (3; M$^+$), 104 (33; $C_8H_8^+$), 96 (55), 91 (73), 79 (100), 67 (47), 41 (48), 39 (57), 27 (36).

$C_{10}H_{14}O$ (150.2) (mixture **2a,b**) Calcd. C 79.96 H 9.39
Found C 79.62 H 9.58

(1'α,2'α,4'α,5'α)-Spiro[cyclopropane-1,6'-[3]oxatricyclo[3.2.2.0^{2,4}]-nonane] (**2a**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.3–0.5 (m; 4H, cyclopropyl-H), 1.1–1.2 (m; 1H), 1.2–1.8 (m; 6H), 2.17 (m_c; 1H, 1'-H), 3.29 (ddd, $J_{4',2'}$ = $J_{4',5'}$ = 4.5 Hz, $J_{4',8a'}$ = 0.75 Hz; 1H, 4'-H), 3.33 (ddd, $J_{2',4'}$ = $J_{2',1'}$ = 4.5 Hz, $J_{2',9a'}$ = 0.75 Hz; 1H, 2'-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 11.78 and 14.94 (two t; C-2, C-3), 17.89 (s; C-1), 22.59 and 23.11 (two t; C-8', C-9'), 29.68 (d; C-1'), 35.87 (t; C-7'), 38.46 (d; C-5'), 53.28 and 53.59 (two d; C-2', C-4').

(1'α,2'β,4'β,5'α)-Spiro[cyclopropane-1,6'-[3]oxatricyclo[3.2.2.0^{2,4}]-nonane] (**2b**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.09 (m; 1H, cyclopropyl-H), 0.2–0.5 (m; 3H, cyclopropyl-H), 1.1–1.2 (m; 2H), 1.5–1.8 (m; 5H), 2.17 (m_c; 1H, 1'-H), 3.21 (m_c; 2H, 2'-H, 4'-H). – ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 13.36 and 15.67 (two t; C-2, C-3), 18.12 (s; C-1), 22.01 and 22.32 (two t; C-8', C-9'), 28.70 (d; C-1'), 35.45 (t; C-7'), 38.56 (d; C-5'), 51.51 and 52.70 (two d; C-2', C-4'). – ^{13}C NMR ($CDCl_3$, 100.6 MHz) of the mixture **2a,b** containing 125 mg of Eu(fod)$_3$[7]: δ = 31.48 (d; C-1', **2a**, Δδ = 2.16), 29.80 (d; C-1', **2b**, Δδ = 1.18), 40.12 (d; C-5', **2a**, Δδ = 1.70), 39.60 (d; C-5', **2b**, Δδ = 1.12), 20.04 (s; C-6', **2a**, Δδ = 2.34), 19.61 (s; C-6', **2b**, Δδ = 1.54), 36.57 (t; C-7', **2a**, Δδ = 0.79), 36.85 (t; C-7', **2b**, Δδ = 1.47), 24.67 (t; C-8', **2a**, Δδ = 2.14), 22.31 (t; C-8', **2b**, Δδ = 0.36), 25.07 (t; C-9', **2a**, Δδ = 2.03), 22.62 (t; C-9', **2b**, Δδ = 0.36). – Δδ are the differences between the chemical shifts of **2a,b** containing 125 mg of Eu(fod)$_3$ minus the shifts of **2a,b** without addition of Eu(fod)$_3$.

Reaction of **1** *with p-Toluenesulfenyl Chloride:* To a solution of 60.0 mg (0.45 mmol) of **1** in 15 ml of CH_2Cl_2 was added dropwise a solution of 71.3 mg (0.45 mmol) of *p*-toluenesulfenyl chloride in 2 ml of CH_2Cl_2. After stirring for 30 min at room temp. and roto-evaporation of the solvent, kugelrohr distillation at 165–170°C/0.2 Torr gave 99 mg (75%) of a colorless oil, consisting of a mixture of the four possible 1,2-*trans* adducts **4**, as confirmed by NMR. It was not possible to separate these isomers, even not by GC, so that the characterization refers to the mixture. – IR (CCl_4): 3090 cm^{-1}, 3010, 2960, 2890, 1499, 1472, 1455, 1095, 1020, 975. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.18–0.56 (m; 10H), 0.74–1.00 (m; 2H), 1.32–2.08 (m; 24H), 2.34 (br. s; 9H, CH_3), 3.43 (m_c; 1H, C*H*SAr), 3.56 (m_c; 1H, C*H*SAr), 3.71 (m_c; 1H, C*H*SAr), 4.01 (m_c; 1H, C*H*Cl), 4.08 (m_c; 1H, C*H*Cl), 4.21 (m_c; 1H, C*H*Cl), 7.01–7.18 (m; 6H, phenyl-H), 7.32–7.42 (m; 6H, phenyl-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 12.12 (t), 14.58 (t), 14.72 (t), 16.13 (t), 18.41, 18.49, 21.02 (t), 24.83, 25.68, 25.77, 31.38 (t), 32.54 (d), 35.59 (d), 36.05 (d), 37.75 (t), 40.35 (d), 40.76 (d), 44.27 (d), 57.27 (d; CSAr), 57.89 (d; CSAr), 59.47 (d; CSAr), 64.81 (d; CHCl), 65.19 (d; CHCl), 67.05 (d; CHCl), 129.70, 131.08, 131.53, 131.99, 132.13, 132.50, 136.80, 137.20 and 137.60. – MS (70 eV): *m/z* (%) = 295 (0.9, M$^+$ + 2), 294 (6, M$^+$ + 1), 293 (3, M$^+$), 292 (15, M$^+$ – 1), 257 (7, M$^+$ – HCl$^+$), 133 (47), 124 (54, ArSH), 105 (47), 91 (100; Ar), 79 (45), 77 (32), 32 (97, S$^+$).

$C_{17}H_{21}ClS$ (292.8) Calcd. C 69.72 H 7.23
Found C 69.70 H 7.26

Reaction of Bicyclo[2.2.2]oct-2-en-5-one with p-Toluenesulfenyl Chloride: To a solution of 800 mg (6.55 mmol) of bicyclooctenone in 20 ml of $CHCl_3$ was added dropwise while stirring 1.04 g (6.55 mmol) of sulfenyl chloride in 10 ml of $CHCl_3$. The yellow reaction mixture was stirred for 12 h at ca. 20°C, then the solvent was roto-evaporated and centrifugal chromatography (Chromatotron; 2-mm discs) on silica gel, eluting with 4:1 petrol ether/methylene chloride, gave 1.49 g (82%) of the isomeric 1,2-*trans* adducts **5a,b** in a 62:38 ratio, respectively. The main isomer **5a** was the second eluate and was obtained as colorless powder, m.p. 94–97°C (chloroform). – IR (CCl_4): 2990 cm^{-1}, 2960, 2900, 1760, 1510, 1480, 1420, 1345, 1290, 1120, 1085. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 1.40–1.50 (m; 1H), 1.9–2.1 (m; 2H), 2.20 (m_c; 1H), 2.32 (m_c; 1H), 2.34 (s; 3H, CH_3), 2.39 (m; 2H), 2.62 (br. dd, $J_{1,7}$ = 6.4 Hz, $J_{1,6}$ = 3.0 Hz; 1H, 1-H), 3.66 (m_c; 1H, 5-H), 4.15 (dt, $J_{6,1}$ = $J_{6,5}$ = 3.0 Hz, J = 0.86 Hz; 1H, 6-H), 7.15 (br. d, J = 8.2 Hz; 2H, phenyl-H), 7.41 (br. d, J = 8.2 Hz; 2H, phenyl-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 18.42 (t), 21.13 (q; CH_3), 22.28 (t), 33.57 (d; C-4), 44.38 (t; C-3), 51.23 (d; C-1), 57.11 (d; C-5), 60.81 (d; C-6), 129.88 (s), 130.03 (d), 132.88 (d), 138.15 (s), 209.82 (s; C=O). – MS (70 eV): *m/z* (%) = 283 (2,

$M^+ + 2$), 282 (14, $M^+ + 1$), 281 (7, M^+), 280 (39, $M^+ - 1$), 124 (100, ArSH), 93 (57), 91 (49), 79 (57), 77 (42), 65 (15), 45 (22), 28 (13).

$C_{15}H_{17}ClOS$ (280.8) Calcd. C 64.16 H 6.10
Found C 64.30 H 6.05

(exo-5,endo-6)-6-Chloro-5-p-tolylsulfinylbicyclo[2.2.2]octan-2-one (**6a**): To a solution of 410 mg (1.46 mmol) of the isomeric 1,2-*trans* adducts **5a,b** in 30 ml of CH_2Cl_2 was added in portions at 0°C while stirring 554 mg (3.21 mmol) of *m*-CPBA. After stirring for 48 h at room temp. the reaction mixture was washed with saturated aqueous $NaHCO_3$ (1 × 30 ml) and H_2O (2 × 40 ml), dried, and the solvent roto-evaporated. The colorless solid residue was submitted to flash chromatography on silica gel (50:1 adsorbent/substrate ratio), eluting with 10:1 $CHCl_3$/ether. The main isomer **6a** was obtained as first fraction: 150 mg (35%), colorless prisms, m.p. 198–199°C ($CHCl_3$). Its X-ray structure is given in Figure 1 and Tables 1 and 2. – IR (CCl_4): 2960 cm^{-1}, 2880, 1740, 1600, 1490, 1465, 1450, 1400, 1330, 1270, 1190, 1080, 1040, 1015, 800. – ^1H NMR ($CDCl_3$; 400 MHz): δ = 1.4–1.5 (m; 1H), 1.9–2.1 (m; 2H), 2.20 (m_c; 1H), 2.3–2.5 (m; 5H), 2.59 (br. dd, $J_{4,8}$ = 6.5 Hz, $J_{4,5}$ = 3.0 Hz; 1H, 4-H), 2.83 (m_c; 1H, 1-H), 3.17 (m_c; 1H, 5-H), 3.94 (pseudo-t; $J_{6,1} = J_{6,5}$ = 3.5 Hz; 1H, 6-H), 7.35 (br. d, J = 8.2 Hz, 2H, phenyl-H), 7.65 (br. d, J = 8.2 Hz; 2H, phenyl-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 18.64 (t), 21.41 (q; CH_3), 22.25 (t), 29.36 (d; C-4), 44.12 (t; C-3), 50.49 (d; C-1), 52.85 (d; C-5), 72.39 (d; C-6), 125.57 (d), 130.17 (d), 137.72 (s), 142.97 (s), 209.06 (s; C=O). – MS (70 eV): *m/z* (%) = 299 (0.2, $M^+ + 2$), 298 (0.5, $M^+ + 1$), 297 (0.5, M^-), 296 (1, $M^+ - 1$), 140 (100), 93 (35), 91 (22), 79 (39), 65 (10).

$C_{15}H_{17}ClO_2S$ (296.8) Calcd. C 60.71 H 5.77
Found C 60.50 H 6.02

Trifluoroacetic Acid-Catalyzed Reaction of **2a**: To a solution of 140 mg (0.93 mmol) of **2a** in 10 ml of CCl_4 was added dropwise at 0°C while stirring 106 mg (0.93 mmol) of trifluoroacetic acid. After stirring for 10 min at 0°C, 10 ml of H_2O was added and the organic phase separated, washed with saturated aqueous $NaHCO_3$ solution, and dried. The solvent was roto-evaporated and the yellow product purified by kugelrohr distillation at 150–155°C/0.1 Torr: 196 mg (80%) of a colorless oil. Capillary GC [50-m Carbowax 20 M glass column, operated at column, injector, and detector temp. of 150, 200, 220°C, respectively, and a carrier gas pressure (N_2) of 1.0 kg/cm²] showed that the distillate consisted of a 65:35 mixture of the hydroxy esters **7a,b**. By means of flash chromatography on silica gel [50:1 adsorbent/substrate ratio, eluting with 6:1 petroleum ether (30–70°C)/ethyl acetate] the isomers were separated, affording **7b** as first fraction: 112 mg (46%) of colorless plates, m.p. 82–83°C (*n*-heptane). The second fraction consisted of **7a**: 40 mg (16%), b.p. 150–160°C/0.1 Torr, colorless wax.

(1α,7β,anti-9)-7-(Trifluoroacetoxy)tricyclo[5.2.1.0^{4,8}]decan-9-ol (**7b**): IR (CCl_4): 3640 cm^{-1}, 2960, 2915, 2895, 1795, 1390, 1235, 1185, 1170, 1050. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.21–1.31 (m; 1H), 1.44 (br. ddd, J' = 12.5 Hz, J'' = 9.5 Hz, J''' = 4.5 Hz; 1H), 1.6–2.1 (m; 11H), 2.22 (ddd, J' = 12.5 Hz, J'' = 9.5 Hz, J''' = 4.5 Hz; 1H), 3.58 (pseudo-t, $J_{9,1} = J_{9,8}$ = 3.8 Hz; 1H, 9-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.64 (t), 16.95 (t), 27.83 (t), 31.35 (d), 36.58 (t), 39.63 (t), 40.15 (d), 43.79 (d), 76.65 (d; C-9), 89.47 (s; C-7), 118.00 (q; CF_3), 157.60 (q; C=O). – MS (70 eV): *m/z* (%) = 264 (0.2, M^-), 246 (0.5, $M^+ - H_2O$), 179 (3, $M^- - COCF_3$), 150 (100, $C_{10}H_{14}O^+$), 132 (41), 119 (51), 117 (31), 104 (32), 91 (60), 79 (32), 28 (47).

$C_{12}H_{15}O_3F_3$ (264.2) Calcd. C 54.55 H 5.72
Found C 54.43 H 5.78

(1α,2β,6β)-6-(Trifluoroacetoxy)tricyclo[4.3.1.0^{3,7}]decan-2-ol (**7a**): IR (CCl_4): 3620 cm^{-1}, 2950, 2880, 1780, 1370, 1220, 1160, 1170, 1090, 970. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.11 (m_c; 1H), 1.35 (m_c; 1H), 1.51 (m_c; 1H), 1.7–1.8 (m; 2H), 1.8–1.9 (m; 2H), 2.0–2.2 (m; 4H), 2.39 (m_c; 1H), 2.5–2.6 (m; 2H), 4.30 (pseudo-t, $J_{2,1} = J_{2,3}$ = 5.0 Hz; 1H, 2-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 21.98 (t), 22.62 (t), 32.95 (d), 33.08 (t), 36.51 (d), 37.63 (t), 43.72 (t), 54.58 (d), 71.78 (d; C-2), 96.90 (s; C-6), 115.94 (q; CF_3), 158.00 (q; C=O). – MS (70 eV): *m/z* (%) = 264 (0.06, M^+), 246 (1, $M^+ - H_2O$), 179 (6, $M^+ - COCF_3$), 150 (100, $C_{10}H_{14}O^+$), 132 (30), 108 (34), 96 (41), 95 (59), 91 (42), 79 (47), 69 (28), 41 (32), 28 (23).

$C_{12}H_{15}O_3F_3$ (264.2) Calcd. C 54.55 H 5.72
Found C 54.47 H 5.61

(1α,7β,anti-9)-Tricyclo[5.2.1.0^{4,8}]decane-7,9-diol (**8b**): A solution of 100 mg (0.38 mmol) of **7b** and 44.8 mg (0.80 mmol) of KOH in 5 ml of ethanol was stirred at room temp. for 48 h. The yellow reaction mixture was poured into 100 ml of H_2O, extracted with ethyl acetate (3 × 10 ml), dried, and the solvent roto-evaporated. The crude 7,9-diol **8b** was recrystallized from chloroform, yielding 20 mg (31%) of colorless needles, m.p. 205–208°C (decomp.). – IR (KBr): 3300 cm^{-1}, 2940, 2860, 1460, 1440, 1360, 1340, 1135, 1070, 1035, 875, 800. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.8–0.9 (m; 1H), 1.2–1.3 (m; 3H), 1.5–2.0 (m; 11H), 3.54 (pseudo-t, $J_{9,1} = J_{9,8}$ = 4.2 Hz; 1H, 9-H). – ^{13}C NMR (DMSO, 100.6 MHz): δ = 15.07 (t), 17.56 (t), 27.60 (t), 31.39 (d), 40.36 (d), 41.40 (t), 42.16 (t), 44.64 (d), 75.73 (s; C-7), 75.98 (d; C-9). – MS (70 eV): *m/z* (%) = 169 (4, $M^+ + 1$), 168 (36, M^+), 150 (34, $M^+ - H_2O$); 110 (100, $M^+ - C_3H_6O^+$), 108 (47), 96 (59), 95 (37), 83 (36), 55 (33), 43 (34). – High resolution MS: *m/z* = 168.1150 (Calcd. for $C_{10}H_{16}O_2$ 168.11503).

(1α,2β,6β)-Tricyclo[4.3.1.0^{3,7}]decane-2,6-diol (**8a**): A solution of 50 mg (0.19 mmol) of **7a** and 22.4 mg (0.40 mmol) of KOH in 3 ml of ethanol was stirred at room temp. for 48 h. The reaction mixture was poured into 10 ml of H_2O, extracted with ethyl acetate (3 × 10 ml), and dried. The solvent was roto-evaporated, yielding 29 mg (94%) of a colorless solid, which on recrystallization from chloroform afforded colorless needles, m.p. 163–164°C (decomp.). – IR (KBr): 3300 cm^{-1}, 2940, 2860, 1360, 1330, 1300, 1095, 1070, 1050, 1020, 1010. – ^1H NMR (DMSO; 400 MHz): δ = 1.0–1.1 (m; 1H), 1.2–1.4 (m; 2H), 1.56 (d, J = 13.8 Hz; 1H), 1.7–2.1 (m; 8H), 2.2–2.3 (m; 1H), 4.16 (br. pseudo-t, $J_{2,1} = J_{2,3}$ = 4.5 Hz; 1H, 2n-H), 4.46 (s; 1H, 6-OH), 4.67 (br. d, $J_{OH,2}$ = 3.6 Hz; 1H, 2-OH). – ^{13}C NMR (DMSO; 100.6 MHz): δ = 22.56 (t), 23.83 (t), 31.66 (t), 33.78 (d), 36.37 (d), 40.85 (t), 46.46 (t), 55.83 (d), 71.21 (d; C-2), 83.37 (s; C-6). – MS (70 eV): *m/z* (%) = 169 (0.5, $M^+ + 1$), 168 (7, M^+), 150 (97, $M^+ - H_2O$), 108 (53), 106 (100), 95 (58), 83 (62), 79 (78), 67 (36), 55 (35, $C_3H_3O^+$), 41 (51, $C_3H_5^+$), 18 (38, H_2O^+).

$C_{10}H_{16}O_2$ (168.2) Calcd. C 71.39 H 9.59
Found C 71.25 H 9.33

CAS Registry Numbers

1: 106988-55-0 / **2a**: 106988-56-1 / **2b**: 107079-25-4 / **3a**: 107079-23-2 / **3b**: 107079-24-3 / **4** (isomer 1): 106988-57-2 / **4** (isomer 2): 106988-58-3 / **4** (isomer 3): 107079-26-5 / **4** (isomer 4): 107079-27-6 / **5a**: 106988-59-4 / **5b**: 107079-28-7 / **6a**: 106988-60-7 / **7a**: 106988-62-9 / **7b**: 106988-61-8 / **8a**: 106988-64-1 / **8b**: 106988-63-0 / CH_2I_2: 75-11-6 / CF_3CO_2H: 76-05-1 / Me-*p*-C_6H_4SCl: 933-00-6 / 1,3-cyclohexadiene: 592-57-4 / methylenecyclopropene: 6142-73-0 / 5-methylenebicyclo[2.2.2]oct-2-ene: 19386-05-1 / bicyclo[2.2.2]oct-2-en-5-one: 2220-40-8

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