Transannular Ring Expansion in the Acid-Catalyzed Reaction of the Oxirane Derived from Spirocyclopropane-Substituted Bicyclo[3.2.1]octene

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In the reaction of spirocyclopropane-, oxo-, and dioxolane-substituted bicyclo[3.2.1]octenes 2a, b, 7a, 7b with arenesulfenyl chloride the *endo*-3-chloro-*exo*-4-arylthio addition products 6a, b, 8a, b, and 10 were formed regio- and stereoselectively. The stereochemistry of 10 was established by X-ray structure determination. In the case of spiro[bicyclo[3.2.1]oct-3-ene-6,1′-cyclopropane] (2a), reaction with arenesulfenyl chloride gave no transannular ring expansion of the spirocyclopropane substituent with or without skeletal rearrangement. However, with trifluoroacetic acid spiro[cyclopropane-1,8′-[3]oxatricyclo[4.2.1.0^{2,4}]nonane] (3a) gave the desired 3,8-disubstituted isotwistane 12a as main product, besides the possible 1,2-*trans* adducts. The structure of the latter was established by an X-ray structure determination of its 3,8-diol 12b. As an additional side product spiro[2.5]oct-6-ene-4-acetaldehyde (14) was formed. Epoxidation of spiro-[bicyclo[3.2.1]octa-3,6-diene-2,1′-cyclopropane] with equimolar *m*-chloroperbenzoic acid (*m*-CPBA) led preferentially to spiro[cyclopropane-1,5′-[3]oxatricyclo[4.2.1.0^{2,4}]non-7-ene] (4a) with traces of the 7′,8′-monoepoxide. Excess *m*-CPBA gave the bisepoxide spiro[cyclopropane-1,5′-[3,8]dioxatetracyclo-[4.3.1.0^{2,4}.0^{7,9}]decane] (5a), which with trifluoroacetic acid afforded the epoxy ketone spiro[cyclopropane-1,6′-[3]oxatricyclo[3.3.1.0^{2,4}]nonan]-8′-one (5b) as minor product and the regio- and stereoselective 1,2-*trans* adduct *endo*-8′-(trifluoroacetoxy)spiro[cyclopropane-1,6′-*exo*-[3]oxatricyclo[3.3.1.0^{2,4}]-nonan]-*exo*-7′-ol (15) as major product, the latter being formed regio- and stereoselectively. Neither 5b nor 15 led to transannular ring expansion of the spirocyclopropane substituent on treatment with trifluoroacetic acid.

Transannulare Ringerweiterung bei der säurekatalysierten Reaktion des Oxirans eines Spirocyclopropan-substituierten Bicyclo-[3.2.1]octens

In den Reaktionen der Spirocyclopropan-, Oxo- und Dioxolan-substituierten Bicyclo[3.2.1]octene **2a, b, 7a, 7b** mit Arensulfenylchlorid wurden regio- und stereoselektiv nur die *endo*-3-Chlor-*exo*-4-arylthio-Additionsprodukte **6a, b** und **8a, b** sowie **10** gebildet. Die Stereochemie von **10** wurde anhand einer Röntgenstrukturanalyse bewiesen. Bei Spiro[bicyclo[3.2.1]oct-3-en-6,1′-cyclopropan] (**2a**) wurden mit Arensulfenylchlorid keine transannularen Ringerweiterungen des Spirocyclopropan-Substituenten mit oder ohne Gerüstumlagerung beobachtet. Jedoch führte Spiro[cyclopropan-1,8′-[3]oxatricyclo[4.2.1.0^{2,4}]nonan] (**3a**) mit Trifluoressigsäure neben den möglichen 1,2-*trans*-Additionsprodukten zum gewünschten 3,8-disubstituierten Isotwistan **12a** als Hauptprodukt, dessen Struktur anhand des 3,8-Diols **12b** durch Röntgenstrukturanalyse belegt wurde. Ein weiteres Nebenprodukt war Spiro[2.5]oct-6-en-4-acetaldehyd (**14**). Epoxidierung von Spiro[bicyclo[3.2.1]octa-3,6-dien-2,1′-cyclopropan] mit *m*-Chlorperbenzoesäure (*m*-CPBA) (äquimolar) führte bevorzugt zum Monoepoxid Spiro[cyclopropan-1,5′-[3]oxatricyclo-[4.2.1.0^{2,4}]non-7-en] (**4a**), nicht jedoch zur gewünschten Epoxidierung an der 7′,8′-Doppelbindung. Überschuß an *m*-CPBA lieferte das Bisepoxid Spiro[cyclopropan-1,5′-[3,8]dioxatetracyclo-[4.3.1.0^{2,4}.0^{7,9}]decan] (**5a**), welches mit Trifluoressigsäure das Epoxyketon Spiro[cyclopropan-1,6′-[3]oxatricyclo[3.3.1.0^{2,4}]-nonan]-8′-on (**5b**) als Nebenprodukt und das 1,2-*trans*-Additionsprodukt *endo*-8′-(Trifluoracetoxy)spiro[cyclopropan-1,6′-*exo*-[3]-oxatricyclo[3.3.1.0^{2,4}]nonan]-*exo*-7′-ol (**15**) als Hauptprodukt lieferte, welches regio- und stereoselektiv gebildet wurde. Weder **5b** noch **15** zeigten mit Trifluoressigsäure eine transannulare Ringerweiterung des Spirocyclopropan-Substituenten.

In the preceding paper[1] it was shown that under appropriate conditions epoxides such as spirocyclopropane-substituted bicyclo[2.2.2]oct-2-ene oxides undergo acid-catalyzed transannular ring expansion with (major product) and without (minor product) skeletal rearrangement, affording complex tricyclic structures such as disubstituted homobrendanes and isotwistanes. It was of interest to extend this novel spirocyclopropane participation to the bicyclo-[3.2.1]octenes. Skeletal rearrangements in the bicyclo[3.2.1] ring system are well documented, leading to complex products that are derived from the interconverting cations shown in Eq. (1)[2].

In the present context of transannular ring expansion[1] the behavior of the spirocyclopropane-substituted bicyclo-[3.2.1]octyl cations **A, B** was to be investigated. Herein we describe our results, using either arenesulfenyl chloride ad-

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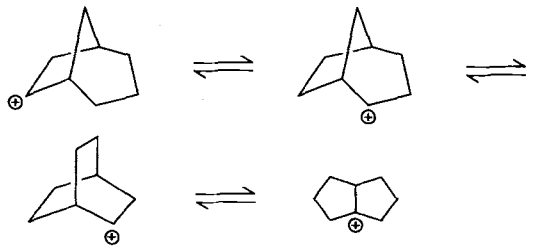
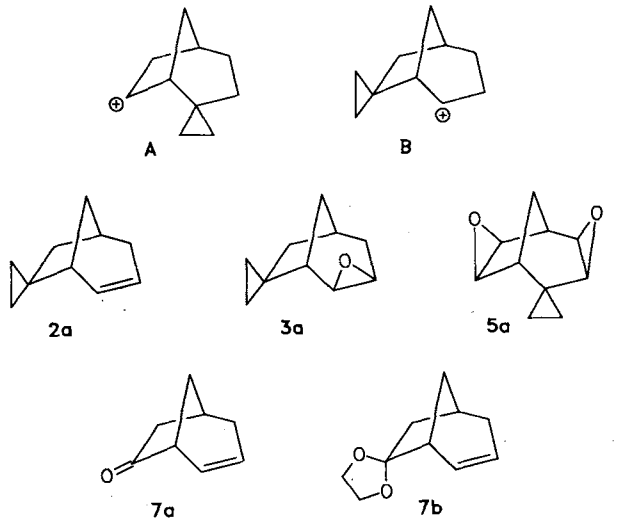


(1)

dition to the corresponding bicyclo[3.2.1]octenes or trifluoroacetic acid-catalyzed reaction of their oxides. As substrates served the olefins and the oxides **2a**, **3a**, **5a**, **7a**, and **7b**.



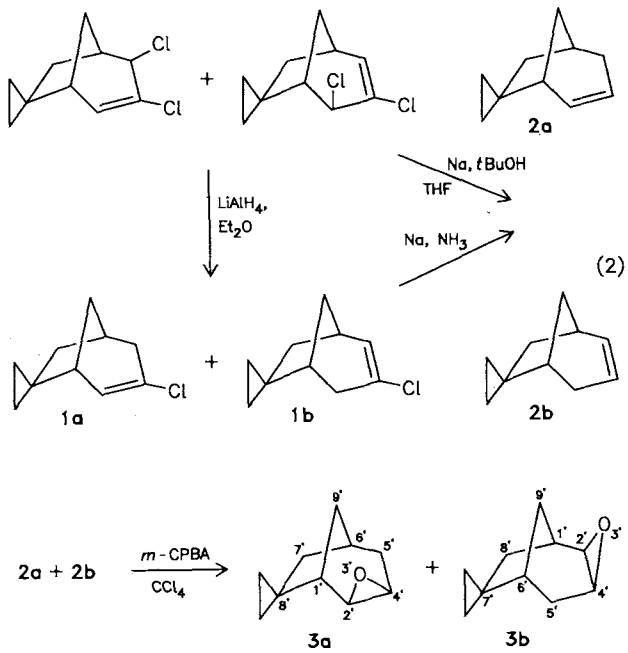
Results

Preparation of Starting Materials

In the synthetic sequence of Eq. (2) is summarized the preparation of the isomeric spiroalkenes **2a**, **b** and their oxides **3a**, **b** starting from the known dichlorides. Either direct exhaustive reductive dechlorination with sodium and *tert*-butyl alcohol[3,4] or stepwise reduction[3] with $LiAlH_4$ to the isomeric chlorides **1a**, **b**, followed by reduction with sodium in liquid ammonia, afforded the isomeric spiroalkenes **2a**, **b**. The direct exhaustive dechlorination is preferred (63% yield). Although these spiroalkenes are known, they have been prepared by a different route[5]. It was not possible to separate by preparative GC the two isomeric olefins **2a**, **b**, neither the dichlorides nor the chlorides **1a**, **b**.

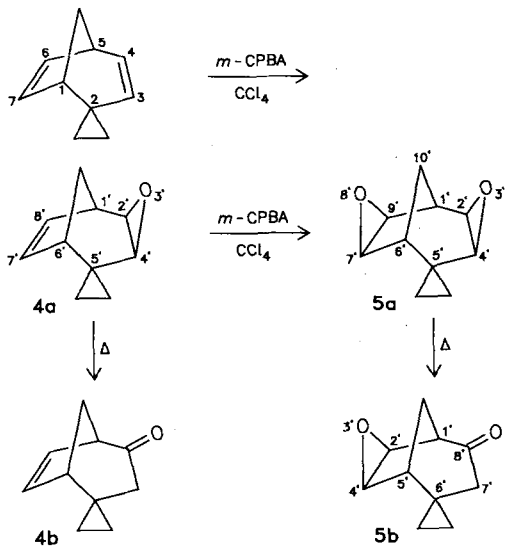
Epoxidation of the isomeric spiroalkenes **2a**, **b** with *m*-chloroperbenzoic acid (*m*-CPBA) in CCl_4 at 0°C afforded the mixture of epoxides **3a**, **b** in 61% yield. Again, neither flash chromatography nor capillary GC was successful in separating the isomers **3a**, **b**; they were characterized as mixture and used as such.

Synthetic access to bicyclo[3.2.1]oct-6-enes with adjacent spirocyclopropane substitution in the trimethylene bridge is cumbersome and we opted for using the readily available spiro[bicyclo[3.2.1]octa-3,6-diene-2,1′-cyclopropane][6] as starting point.



(2)

The results are collected in the preparative sequence of Eq. (3). Partial epoxidation with stoichiometric amounts of *m*-CPBA in CCl_4 at room temperature led preferentially to the monoepoxide **4a** in 9% yield, which could be isolated in pure form by means of flash chromatography on silica gel. Attempted purification by means of preparative GC (injector temperature ca. 200°C) led to the isolation of the ketone **4b** in 40% yield.



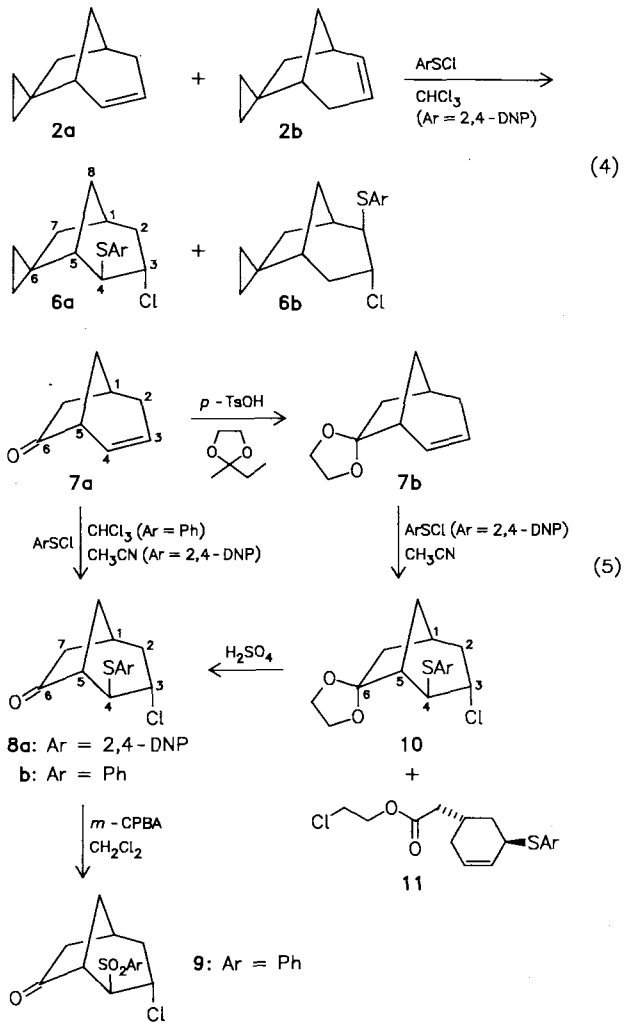
(3)

With an excess of *m*-CPBA on the spirodiene (Eq. 3) in CCl_4 at room temperature the bisepoxide **5a** was isolated in 36% yield, but attempts to obtain an analytically pure sample of **5a** failed. Preparative GC (injector temperature ca. 190°C) afforded the pure epoxy ketone **5b**, isolated in 43% yield.

Transformations

The addition of 2,4-dinitrobenzenesulfenyl chloride (ArSCl) to the isomeric mixture of spiroalkenes **2a, b** gave

only the two respective chloro sulfides **6a, b**. The fact that only these two isomers were formed, i.e. **6a** from **2a** and **6b** from **2b**, was established by HPLC and by ^{1}H NMR (400 MHz). In **6a**, the aromatic 3-H and 6-H protons are located characteristically at δ = 9.08 and 7.63 as double peaks. By means of flash chromatography on silica gel isomer **6a** was obtained in pure form. That no transannular ring expansion by the remote spirocyclopropane moiety had taken place (with or without skeletal rearrangement) was established by reductive dechlorination and desulfurization of the crude reaction mixture **6a, b** with sodium in liquid ammonia[7]. A 1:1 isomeric mixture of the spiroalkenes **2a, b** was obtained, with no traces of other products (besides the spiroalkane derived from **2a, b**) in the capillary gas chromatogram. This pronounced regio- and stereoselectivity was surprising, especially in view of the homologous spirobicyclo[2.2.2]octene[1], which gave all four possible 1,2-*trans* adducts with arenesulfenyl chloride. For comparison we examined the electrophilic addition of arenesulfenyl chlorides to bicyclo[3.2.1]oct-3-en-6-one (**7a**) and its acetal **7b**. These transformations are displayed in Eq. (5).



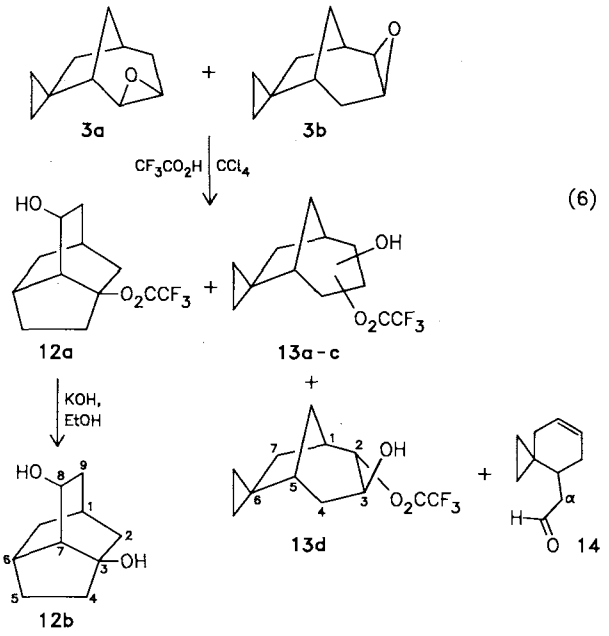
(4)

(5)

Addition of arenesulfenyl chloride to the enone **7a** (Eq. 5) gave as major products the 1,2-*trans* adducts **8a, b** for benzenesulfenyl chloride (in $CHCl_3$) and 2,4-dinitrobenzenesulfenyl chloride (in CH_3CN) in 75 and 84% yields, respectively.

Since it was difficult to assign the regio- and stereochemistry on spectral data (NMR) alone, the chloro sulfide **8b** was oxidized with *m*-CPBA in CH_2Cl_2 to its sulfone **9**. It was hoped to elucidate the structure of the latter by means of X-ray analysis, but the crystals were not suitable. For this reason, the enone **7a** was converted to its acetal **7b** by *p*-toluenesulfonic acid-catalyzed reaction with the 1,3-dioxolane of 2-butanone. Electrophilic addition of 2,4-dinitrobenzenesulfenyl chloride to **7b** in CH_3CN gave two products, namely the 1,2-*trans* adduct **10** (71% isolated) and the ring-opened cyclohexenyl derivative **11** (3% isolated), using centrifugal chromatography on silica gel. The structure of the chloro sulfide **10** was established by X-ray analysis (Figure 1; Tables 1 and 2). The structure of **11** was established by means of spectral data. A precedent for such ring-opened product has been reported[8]. Furthermore, acid-catalyzed hydrolysis of the chloro sulfide **10** gave **8a**, which was identical to that derived from the enone **7a**. With this chemical correlation, the regio- and stereochemistry of the electrophilic addition of arenesulfenyl chlorides is rigorously defined.

The trifluoroacetic acid-catalyzed reaction of the spiro epoxides **3a, b** was complex (TLC at least six spots), in part due to the fact that the mixture of isomers had to be used, since attempted chromatographic separation failed. The results are given in Eq. (6).



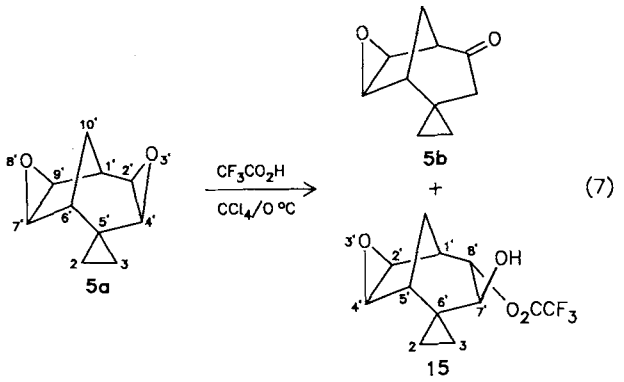
(6)

Flash chromatography on silica gel gave four fractions of different products (by TLC), of which the major one (26% isolated, third fraction) corresponded to the disubstituted isotwistane **12a**. Its structure was established by hydrolysis to the 3,8-diol **12b** and X-ray analysis of the latter (Figure 1; Tables 1 and 3).

The addition products, i.e. the hydroxy esters **13a–d**, were obtained in two fractions, the second one consisting of

a complex mixture (by TLC) of the three isomers **13a–c** (6% isolated) and the pure isomer **13d** (2% isolated) as the fourth fraction. NOE differential ^{1}H-NMR spectroscopy was helpful in this assignment (cf. Figure 2). The ring-cleavage product, i.e. the aldehyde **14** (6%), eluted as first fraction in the flash chromatography. The structures of these products rest on spectral data (cf. Experimental Section). No evidence for disubstituted homobrendanes could be obtained from the crude reaction mixture of the acid-catalyzed reaction of the spiro epoxides **3a, b**.

The trifluoroacetic acid-catalyzed treatment of the bisepoxide **5a** led to rearranged ketone **5b** (also formed in the attempted GC purification of the bisepoxide, cf. Eq. 3) and the intact hydroxy ester **15** (Eq. 7). These were isolated by means of flash chromatography on silica gel. The rearranged ketone **5b** eluted first as minor product (8%) and the hydroxy ester **15** subsequently as major product (49%), both characterized by their spectral data (cf. Experimental Section).



(7)

Structure Assignments

The NMR spectral data for most of the new substances reported here are exceedingly complex and without the help of X-ray analysis (Figure 1) of the chloro sulfide **10** and 3,8-dihydroxyisotwistane (**12b**) it would have been difficult to make definitive assignments. In addition, extensive ^{1}H-NMR decoupling experiments were essential to confirm the proposed structures. These are given in the Experimental Section for the new compounds **4a, b, 5a, b, 8a, b, 11, 13d**, and **15** and will not be further elaborated here.

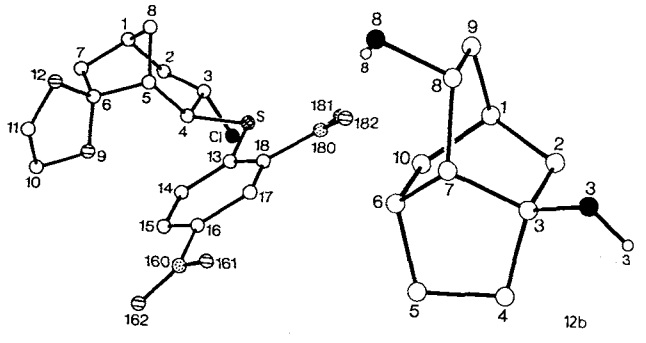


Figure 1. Perspective drawings of the molecular structures of the chloro sulfide **10** and 3,8-dihydroxyisotwistane (**12b**). In the case of **10**, open circles are carbon atoms, the solid circle is a chlorine atom, the chequered a sulfur atom, the dotted a nitrogen atom, and the parallel-lined are oxygen atoms; for **12b** the open circles are carbon and the solid ones oxygen atoms

The general trends and concordance is evident for these very similar structures of compounds **6a, b, 8a, b, 9**, and **10**. The characteristic and definitive resonances are those of the protons 3x-H (broad doublet) and 4n-H (broad singlet) and the doublets of carbon atoms, C-3 and C-4, to which the chloro and arylthio substituents are bound, respectively. The large difference in the chemical shifts between the bridgehead protons 1-H and 5-H in the spiroalkene adduct **6a** is due to the shielding effect of the spirocyclopropane substituent[9] (cf. Experimental Part).

As in the preceding paper[1], the isotwistane derivatives **12a, b** show the characteristic substituted carbons C-3 (s) and C-8 (d) and the characteristic 8-H proton adjacent to the hydroxyl substituent. The C-3 and C-8 ^{13}C-NMR signals are at δ = 90.04 and 63.35 for the hydroxy ester **12a** and δ = 76.13 and 62.14 for the diol **12b**, respectively. The corresponding 8-H protons are located at δ = 4.25 (dt) and 4.06 (ddd) for the hydroxy ester **12a** and the diol **12b**, respectively. The remaining protons overlapped too strongly to employ decoupling experiments for their rigorous assignment; however, the proposed structures are consistent with the available spectral data (cf. Experimental Section).

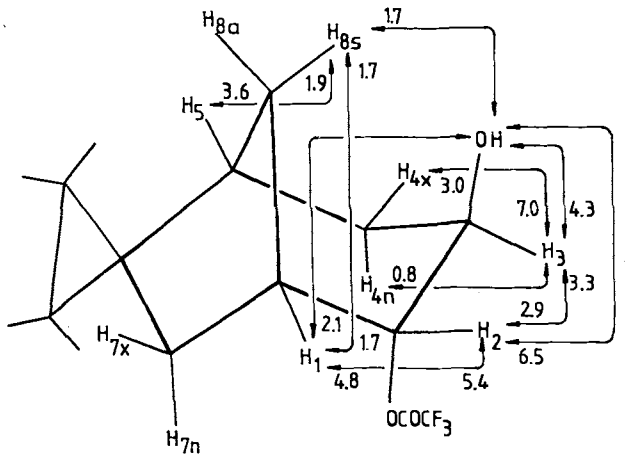


Figure 2. NOE differential ^{1}H-NMR spectroscopy of hydroxy ester **13d**: the enhancements (in %) are given at the tip of the arrows for the interacting protons

In the case of the pure hydroxy ester isomer **13d** NOE experiments (Figure 2) permitted establishing the boat form of the cyclohexane ring as the preferred conformation in solution. A similar conformational preference was also observed for the chloro sulfide adduct **10** (Figure 1) in the crystalline phase. Thus, irradiation of the low-field broad doublet at δ = 4.95 singled out coupled resonances at δ = 2.05 (3.0% enhancement) and δ = 1.77 (0.8%), to be attributed to the 4x-H and 4n-H methylenic protons, respectively. The saturated resonance at δ = 4.95, therefore, pertains to 3-H. On the other hand, saturation of the other low-field resonance at δ = 3.86 (necessarily 2-H) enhanced the bridgehead 1-H absorption at δ = 2.45. Irradiation at this frequency and at the other bridgehead 5-H resonance at δ =

1.43 allowed to individuate the 8a-H proton at $\delta = 1.95$. In carefully dried $CDCl_3$, the hydroxy proton resonates at about $\delta = 4.9$. Selective saturation of the hydroxy proton brought about a small but significant enhancement (1.7%) of the 8s-H proton, suggesting that the cyclohexane ring of this hydroxy ester **13d** prefers the boat conformation. Upon irradiation of the spirocyclopropane resonances, no enhancement was observed for 3-H. For the chair conformation of the cyclohexane ring, the 3-H proton is proximate to some of the spirocyclopropane protons and enhancements should have been observed. Furthermore, the boat conformation is more in accord with the small $J_{2,3}$ coupling constant (1.2 Hz).

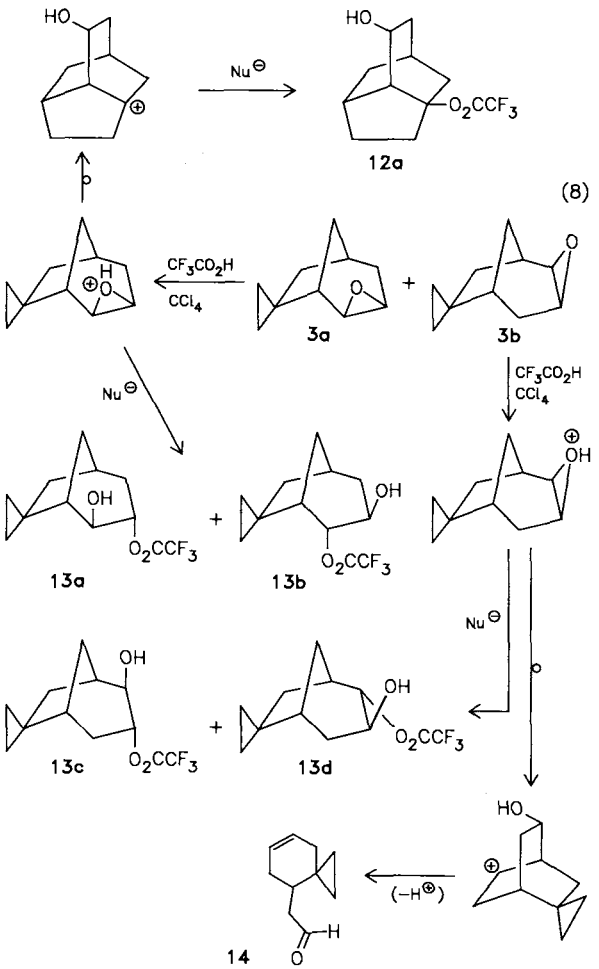
Discussion

The reaction of the spiroalkene **2a, b** with arenesulfenyl chloride afforded only 1,2-*trans* addition, even with the most electrophilic 2,4-dinitrobenzene derivatives (Eq. 4). Not even traces of transannular ring expansion by the remote spirocyclopropane group to disubstituted homobrendanes (no skeletal rearrangement) or isotwistanes (with sketal rearrangement), could be observed.

The same regio- and stereochemistry of the electrophilic addition of arenesulfenyl chloride was also observed for bicyclo[3.2.1]oct-3-en-6-one (**7a**) and acetal **7b** (Eq. 5). This selectivity matches our experiences with the spirocyclo[2.2.1]hept-2-ene system[7], but contrasts with those for the spirobicyclo[2.2.2]oct-2-ene system[1]. Analogous to the norbornene case[7], steric factors are presumably responsible for the preferred *exo* attack of the arenesulfenyl chloride electrophile on the π bond of the bicyclo[3.2.1]octenes, leading to an *exo*-episulfonium ion intermediate. Therewith the observed *exo*-arylthio and *endo*-chloro stereochemistry is defined. The preferred *endo*-3-chloro and *exo*-4-arylthio regiochemistry is derived presumably also from steric effects by the remote spirocyclopropane, oxo, or spirodioxolane moieties on the incoming chloride ion nucleophile.

Be this as it may, from the point of view of transannular ring expansion of the remote spirocyclopropane in the electrophilic addition of arenesulfenyl chloride, the [3.2.1] skeleton behaves analogous to the [2.2.2]skeleton[1], leading exclusively to 1,2-*trans* adducts. This must be contrasted with the [2.2.1] skeleton[7], for which transannular ring expansion is the major course of action. As already explained[1,7], subtle conformational factors in the arrangement of the spirocyclopropane and episulfonium ion rings dictate whether simple 1,2-*trans* addition or complex transannular ring expansion (with or without skeletal rearrangement) prevails. The latter pathway predominates for the norbornane skeleton in view of optimal conformational disposition of the spirocyclopropane moiety, while for the [3.2.1] and [2.2.2] systems nucleophilic trapping by chloride ion prior to skeletal rearrangement and/or transannular ring expansion wins out.

The situation is different, however, in the acid-catalyzed reaction of the spiro epoxides **3a, b**. Analogous to the epoxides of the bicyclo[2.2.2]oct-2-enes[1], the isomer **3a** leads to skeletally rearranged and transannularly ring-expanded 3,8-disubstituted isotwistane **12a** as major product, while the 1,2-*trans* adducts **13a–d** are formed in minor amounts (Eq. 6). These observations are mechanistically rationalized in Eq. (8). In the isomer **3b** the remote spirocyclopropane group is unfavorably disposed towards transannular participation and besides simple 1,2-addition, the aldehyde **14** is produced via skeletal rearrangement and subsequent ring fragmentation. Of the four possible 1,2-adducts **13a–d**, only **13d** could be isolated in pure form and be fully characterized. Clearly, it should pertain to the epoxide **3b**. The remaining three **13a–c** were obtained as inseparable mixture, of which **13a, b** should be derived from epoxide **3a** and **13c** from epoxide **3b**.



Of mechanistic interest is the fact that the 3,7-disubstituted homobrendane is not formed in the trifluoroacetic acid treatment of epoxide **3a**. Consequently, the protonated oxirane first undergoes skeletal rearrangement, followed by transannular ring expansion affording the isotwistane **12a** (Eq. 8). Besides conformational factors, additional driving force for skeletal rearrangement derives from the fact that the isotwistane ring system is by ca. 0.7 kcal/mol less strained than the homobrendane one[10]. Furthermore, of the ring systems in Eq. (1), the [2.2.2]skeleton is favored[11].

Our experiences with the epoxides **4a** and **5a** derived from the spirodiene in Eq. (3) are discouraging from the point of view of transannular ring expansion. The fact that under

stoichiometric epoxidation conditions first the double bond adjacent to the spirocyclopropane ring was epoxidized by *m*-CPBA, precluded obtaining the desired 3,4-epoxy derivative. Saturation of the 6,7-double bond would have afforded the substrate of choice for probing transannular ring expansion namely spiro[cyclopropane-1,6′-[3]oxatricyclo[3.3.1.$0^{2,4}$]nonane]. Furthermore, the fact that also the bisepoxide **5a** rearranged on heating to the oxo epoxide **5b** (Eq. 3), which is analogous to the **4a** → **4b** transformation, indicates that the epoxide ring adjacent to the spirocyclopropane ring is the more reactive one. Presumably cyclopropylcarbinyl stabilization dictates this chemical preference.

Consequently, it should not be surprising that under mild conditions acid-catalyzed reaction of the bisepoxide **5a** with trifluoroacetic acid leads to the rearranged oxo epoxide **5b** and the 1,2-adduct **15** (Eq. 7). If the 2′,4′-epoxide ring is not protonated, transannular participation by the spirocyclopropane moiety cannot be expected. Under forced conditions, both the oxo epoxide **5b** and the hydroxy ester **15** gave undefined, complex product mixtures. Thus, whether the spiro[cyclopropane-1,6′-[3]oxatricyclo[3.3.1.$0^{2,4}$]nonane] participates in transannular ring expansion cannot be answered at this point.

In summary, a delicate balance of conformational and electronic factors appears to determine whether transannular ring expansion by remote spirocyclopropane groups can compete with 1,2-*trans* addition of the electrophilic reagent. Protonated oxiranes tend to participate in transannular ring expansion more dominantly than episulfonium ions. However, the most significant feature for transannular participation appears to be the geometrical proximity of the spirocyclopropane ring and a rigid structure. This is optimally fulfilled for the spironorbornene case[7]. This aspect is more dramatically brought out for flexible monocyclic substrates such as 1-oxadispiro[2.2.2.1]nonane, for which only 1,2-*trans* addition was observed.

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Experimental

Boiling and melting points are uncorrected, the latter were taken on a Reichert Thermovar Kofler apparatus. – Infrared (IR) spectra: Beckman Acculab 4. – ^{1}H-NMR spectra: Varian EM 390 (90 MHz) or Bruker WM 400 (400 MHz), TMS as internal standard. – ^{13}C-NMR spectra: Bruker WH 90 (22.64 MHz) or Bruker WM 400 (100.6 MHz), $CDCl_3$ as internal standard. – Mass spectra (MS): Varian MAT CH 7 or Finnigan MAT 44, coupled with GC. – Combustion analyses: Either obtained in-house or from Prof. G. Maier's staff at the Institut für Organische Chemie (Gießen). – Thin-layer chromatography (TLC): Polygram SIL/G/UV (40 × 80 mm), Macherey and Nagel Co. – Column chromatography: Silica gel 70–230 mesh ASTM (activity III), adsorbent-substrate ratio at least 20:1. – Analytical gas chromatography: Carlo Erba Strumentazione Model 2900 Fractovap Series or Model 4100 instruments, equipped with capillary columns and FID. – Preparative gas chromatography: Carlo Erba Strumentazione Model 4200. – Analytical HPLC: Kontron liquid chromatograph (Pump 414, UV Detector Uvikon 720 LC, Anacomp Computer), supplied with a Lichro Sorb Si 60 (5μm) (250 mm × 4 mm).

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. Unless otherwise stated, stirring was performed magnetically, room temperature was ca. 20°C, drying after aqueous work-up carried out with $MgSO_4$ or Na_2SO_4, and roto-evaporation was performed at aspirator pressure (ca. 20°C at 15–20 Torr).

Nuclear Overhauser Spectroscopy of the Hydroxy Ester **13d**: The NOE experiments were carried out on the Bruker WP200SY instrument. The samples (in $CDCl_3$) were freed from oxygen by sonication under N_2 gas purging. The usual procedure for gated irradiation experiments was modified[12] and the selected resonance was saturated by a 8-s cyclic perturbation of all lines with a 38–40 dB attenuation of a nominal 0.2 W decoupling power. The enhancements (in %) were obtained from the multiplier of the reference spectrum by bringing the observed multiplet to exact matching with the corresponding multiplet in the perturbed spectrum. Errors are ca. 0.3%. By careful choise of the multiplier, in most cases it was possible in the differential mode to single out a pure multiplet from a set of overlapping signals. The NOE results are displayed in Figure 2.

X-ray Crystallography of the Chloro Sulfide **10** *and 3,8-Dihydroxyisotwistane* (**12b**): The orientation matrix and the cell parameters were determined from transparent colorless crystals of given dimensions (Table 1) on a SYNTEX-P3 four-circle diffractometer. Measurement of intensities: ω-scan, 1° range, Mo-K_α, 2Θ maximum = 55°. All reflections with $F \geqq 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL[13] program system on an Eclipse S/250 was employed. All structures could be refined by anisotropic least squares cycles to the given *R* values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. The special X-ray operations and results are listed in Table 1, the positional and thermal parameters in Tables 2 and 3. The structures are exhibited in Figure 1.

Table 1. X-Ray operations and results of the chloro sulfide **10** and 3,8-dihydroxyisotwistane (**12b**)

compound	10	12b
chemical formula	$C_{16}H_{17}N_2O_6SCl$	$C_{10}H_{16}O_2$
molecular mass [amu]	400.833	168.235
a [pm] (esd)	1131.2(5)	692.9(4)
b [pm] (esd)	1655.1(4)	1073.6(7)
c [pm] (esd)	972.6(5)	659.4(3)
α [deg] (esd)		93.96(5)
β [deg] (esd)	107.66(4)	114.95(4)
γ [deg] (esd)		81.39(5)
molecular volume [$cm^3 \cdot mol^{-1}$]	261.268	132.431
no. Z of formular units/cell	4	2
calcd. density [$g \cdot cm^{-3}$]	1.534	1.270
crystal system	monoclinic	triclinic
space group (no.)	$P2_1/n$ (14)	$P\bar{1}$ (2)
crystal size [mm]	0.25x0.5x0.15	0.35x0.55x0.25
no. of measd. intensities	3617	2010
no. of obsd. reflections	2842	1870
no. of struct. factors of direct phase determination	406	425
R ($\Sigma\|\Delta F\|/\Sigma Fo$)	0.046	0.049
R_w	0.043	0.055
no. of refd. parameters	236	117
resid. elect. density [$e \cdot Å^{-3}$]	0.355	0.242

Table 2. Positional ($\times 10^4$) and thermal ($pm^2 \cdot 10^{-1}$) parameters[a] of the atoms of chloro sulfide **10**. For numbering of the atoms cf. Figure 1; the standard deviations are given in parentheses

	x	y	z	U(equiv)
S	1081(1)	6650(1)	2791(1)	48(1)
Cl	-1054(1)	7410(1)	4149(1)	68(1)
C(1)	-2907(2)	6100(2)	540(3)	57(1)
C(2)	-2675(2)	6683(2)	1819(3)	61(1)
C(3)	-1313(2)	6919(2)	2439(3)	46(1)
C(4)	-436(2)	6196(1)	2599(2)	37(1)
C(5)	-849(2)	5629(1)	1270(3)	40(1)
C(6)	-1648(2)	4919(2)	1502(3)	46(1)
C(7)	-2990(3)	5227(2)	1000(3)	63(1)
C(8)	-1767(3)	6066(2)	4(3)	54(1)
O(9)	-1256(2)	4643(1)	2943(2)	60(1)
C(10)	-1347(3)	3787(2)	2881(4)	72(1)
C(11)	-1015(3)	3597(2)	1548(4)	73(1)
O(12)	-1535(2)	4253(1)	622(2)	61(1)
C(13)	2087(2)	5822(1)	3151(2)	40(1)
C(14)	1799(2)	5092(2)	3706(3)	45(1)
C(15)	2586(2)	4438(2)	3976(3)	50(1)
C(16)	3696(2)	4494(2)	3669(3)	48(1)
C(17)	4029(2)	5187(2)	3119(3)	49(1)
C(18)	3244(2)	5846(2)	2890(3)	44(1)
N(160)	4550(2)	3804(1)	3945(3)	65(1)
O(161)	5451(2)	3841(2)	3497(3)	97(1)
O(162)	4347(2)	3244(1)	4649(3)	89(1)
N(180)	3678(2)	6581(2)	2353(2)	59(1)
O(181)	3191(2)	7222(1)	2482(3)	77(1)
O(182)	4517(2)	6511(2)	1810(3)	90(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3. Positional ($\times 10^4$) and thermal ($pm^2 \cdot 10^{-1}$) parameters[a] of the atoms of 3,8-dihydroxyisotwistane (**12b**). For numbering of the atoms cf. Figure 1; the standard deviations are given in parentheses

	x	y	z	U (equiv)
C(1)	-1689(3)	7114(2)	-18(3)	43(1)
C(2)	357(3)	7615(2)	242(3)	46(1)
C(3)	1599(3)	8039(1)	2679(3)	36(1)
O(3)	2335(2)	9226(1)	2744(2)	47(1)
C(4)	3417(3)	7021(2)	4071(3)	51(1)
C(5)	2416(3)	6250(2)	5168(3)	56(1)
C(6)	18(3)	6755(2)	4144(3)	44(1)
C(7)	58(3)	8157(1)	3827(3)	37(1)
C(8)	-2100(3)	8909(2)	2435(3)	43(1)
O(8)	-3442(2)	9090(1)	3626(3)	62(1)
C(9)	-3236(3)	8212(2)	243(3)	52(1)
C(10)	-1181(3)	6160(2)	1811(3)	50(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (West-Germany). These data are available with quotation of the registry number CSD-52654, the authors, and the reference to this publication.

3-Chlorospiro[bicyclo[3.2.1]oct-3-ene-6,1'-cyclopropane] (**1a**) *and 3-Chlorospiro[bicyclo[3.2.1]oct-2-ene-6,1'-cyclopropane]* (**1b**): To a stirred suspension of 1.52 g (40.0 mmol) of $LiAlH_4$ in 50 ml of ether 4.00 g (19.7 mmol) of *exo*-2(4),3-dichlorospiro[bicyclo-[3.2.1]oct-2(3)-ene-6,1'-cyclopropane][3] was added within 30 min at ambient temperature. After 14 h excess $LiAlH_4$ was destroyed by careful addition of 1.50 ml of water, 1.50 ml of 2 N NaOH, and again 4.50 ml of water (CAUTION!), the precipitate was filtered and washed with ether. The filtrate was washed once with 20 ml of sodium chloride solution, dried with $MgSO_4$, and concentrated at 20°C/20 Torr. Distillation provided 2.10 g (63%) of spirocyclopropanes **1a, b** as colorless liquid, b.p. 94–96°C/20 Torr. – IR(CCl_4): 3060 cm^{-1}, 2980, 2920, 2860, 1635, 1380, 1360, 1300, 1045, 635. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 0.4–0.6 (m; 4H, cyclopropane-H), 1.2–2.9 (m; 8H), 5.9–6.1 (m; 1H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.24 (t), 9.95 (t), 16.35 (t), 16.42 (t), 25.77 (t), 30.81 (s), 35.14 (t), 35.60 (d), 35.60 (t), 37.27 (d), 40.97 (t), 41.11 (t), 43.00 (d), 44.12 (d), 44.30 (t), 44.97 (t), 129.87 (d), 130.20 (s), 130.50 (s), 131.33 (d). – MS (70 eV): *m/z* (%) = 170 (7, M^+), 168 (21, M^+), 115 (34), 113 (63), 91 (100), 79 (78).

$C_{10}H_{13}Cl$ (168.7) Calcd. C 71.21 H 7.77
Found C 71.47 H 7.91

Spiro[bicyclo[3.2.1]oct-3-ene-6,1'-cyclopropane] (**2a**) *and Spiro-[bicyclo[3.2.1]oct-2-ene-6,1'-cyclopropane* (**2b**). – *Method A:* At –78°C 3.00 g (0.130 mol) of metallic sodium was dissolved in 100 ml of liquid ammonia with efficient mechanical stirring. 2.00 g (10.7 mmol) of **1a, b** in 5 ml of ether was added and stirring was continued for 5 h at –78°C. The ammonia was allowed to evaporate overnight, the residue was diluted with 75 ml of ether and 20 ml of water was added carefully (CAUTION!). The aqueous layer was extracted with ether (3 × 15 ml), the combined organic layers were washed with 5% aqu. ammonium chloride and sodium chloride solution and dried with $MgSO_4$. The solvent was rotoevaporated (20°C/20 Torr) and the residue distilled to give 364 mg (26%) of **2a, b** as a colorless liquid, b.p. 60–62°C/20 Torr (Lit.[5] 70°C/25 Torr).

Method B[4]: A 50-ml three-necked flask, provided with a reflux condenser and efficient mechanical stirrer, was charged with 5.10 g (0.220 mol) of metallic sodium, 12.6 g (0.100 mol) of *tert*-butyl alcohol, and 100 ml of THF. While stirring, 4.00 g (19.7 mmol) of *exo*-2(4),3-dichlorospiro[bicyclo[3.2.1]oct-2(3)-ene-6,1'-cyclopropane][3] in 10 ml of THF was added and the mixture was vigorously refluxed for 72 h. Excess sodium was destroyed by adding small portions of water (CAUTION!). The reaction mixture was extracted with petroleum ether (30–50°C) (3 × 50 ml), the combined extracts were washed with water and dried with $MgSO_4$. The solvent was rotoevaporated at 20°C/20 Torr and the residue was purified by distillation to give 2.00 g (70%) of **2a, b**.

Capillary GC on a 50-m OV 101 column, operating at column, detector and injector temperatures of 80, 200, and 150°C, respectively, and a carrier gas flow (N_2) of 0.8 ml/min revealed two compounds in a 1:1 ratio (t_{R1} = 1263 s, t_{R2} = 1283 s). Separation on preparative scale using silver nitrate impregnated (1 and 5%) 1.5-m Volaspher A2 column was not successful. Also treatment of the mixture with KO*t*Bu in DMSO in order to enrich one isomer, failed.

Spiro[cyclopropane-1,8'-[3]oxatricyclo[4.2.1.$0^{2,4}$]nonane] (**3a**) *and Spiro[cyclopropane-1,7'-[3]oxatricyclo[4.2.1.$0^{2,4}$]nonane]* (**3b**): To a solution of 1.60 g (11.9 mmol) of spiroolefins **2a, b** in 40 ml of absol. CCl_4 was added ca. 5 mg of solid $NaHCO_3$ and portionwise 3.11 g (18.0 mmol) of *m*-chloroperbenzoic acid (*m*-CPBA) at 0°C, while cooling by an ice bath. After 12 h stirring at room temp. the solid materials were removed by filtration and the filtrate washed with aqu. Na_2SO_3 (2 × 50 ml), aqu. $NaHCO_3$ (2 × 50 ml),

and water (1 × 50 ml) and dried. The solvent was rotoevaporated yielding a yellow oil, which on kugelrohr distillation at 70–80°C/0.1 Torr gave 1.10 g (61%) of **3a, b** as a colorless oil. Capillary GC on a 50-m Carbowax column, operated at detector, injector, and column temperatures of 200, 190, and 80°C, respectively, and a carrier gas (N_2) pressure of 0.5 kg/cm² did not result in the separation of the isomers. – IR(CCl_4): 3070 cm^{-1}, 3000, 2940, 2860, 1435, 1420, 1075, 1010, 970, 910, 870, 850. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.2–0.3 (m; 1H, cyclopropane-H), 0.34–0.41 (m; 1H, cyclopropane-H), 0.41–0.59 (m; 5H, cyclopropane-H), 0.70 (mc; 1H, cyclopropane-H), 1.1–1.2 (m; 1H), 1.4–1.9 (m; 12H), 2.01 (br. dd, $J_{5'n,5'x}$ = 15.0, $J_{5'n,4'}$ = 5.0 Hz; 1H, 5'n-H), 2.1 (m; 1H), 2.54 (br. dd, $J_{1',8'x}$ = 10, $J_{1',2'n}$ = 4.5 Hz; 1H, 1'-H), 2.94 (br. pseudo-t, $J_{2',4'}$ = $J_{2',1'}$ = 4.5, $J_{2',9a'}$ = 1.2 Hz; 1H, 5'-H), 2.98 (br. pseudo-t, $J_{2',4'}$ = $J_{2',1'}$ = 4.5, $J_{2',9a'}$ = 1.2 Hz; 1H, 2'-H), 3.01–3.06 (m; 2H, 3'-, 4'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.51, 10.07, 14.86, and 16.94 (four t; C-2, -3), 23.47 and 25.07 (two s; C-1), 30.63 (t), 30.68 (t), 30.90 (t), 32.87 (d), 33.81 (t), 36.08 (d), 38.48 (t), 39.96 (d), 41.48 (t), 42.48 (d), 49.46 (d), 49.52 (d), 55.01 (d), 56.70 (d). – MS (70 eV): *m/z* (%) = 150 (4; M^+), 106 (58), 91 (100), 79 (95), 67 (43), 41 (47), 39 (47), 28 (18), 27 (33).

$C_{10}H_{14}O$ (150.1) Calcd. C 79.95 H 9.39
Found C 79.57 H 9.52

Spiro[cyclopropane-1,5'-[3]oxatricyclo[4.2.1.0^{2,4}]non-7-ene] (**4a**): To a solution of 1.00 g (7.57 mmol) of spiro[bicyclo-[3.2.1]octa-3,6-diene-2,1'-cyclopropane] in 20 ml of absol. CCl_4 was added ca. 5 mg of solid $NaHCO_3$, followed by portionwise addition of solid *m*-CPBA while stirring and cooling at 0°C by means of an ice bath. After stirring for 5 h at room temp., the solid matter was removed by filtration, the latter washed with aqu. Na_2SO_3 (2 × 50 ml), aqu. $NaHCO_3$ (2 × 50 ml), and water (50 ml) and dried. Rotoevaporation of the solvent gave a yellow oil, which was submitted to kugelrohr distillation at 50–60°C/1.0 Torr, leading to impure monoepoxide **4a**. Flash chromatography on silica gel (adsorbent-substrate ratio 50:1), eluting with petroleum ether (30–70°C)/ethyl acetate (6:1) gave 100 mg (9%) of pure product **4a** as colorless, waxy oil. Attempts to obtain an analytically pure sample of **4a** by preparative GC led to the rearranged ketone **4b**, for which a satisfactory elemental analysis was obtained as given below. – IR($CDCl_3$): 3070 cm^{-1}, 3000, 2940, 1445, 1425, 1335, 1235, 1030, 975, 860, 840. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.4–0.5 (m; 3H, cyclopropane-H), 0.8–0.9 (m; 1H, cyclopropane-H), 1.5–1.6 (m; 2H, 9'a-, 6'-H), 2.11 (d, $J_{9's,9a'}$ = 9.7 Hz; 1H, 9's-H), 2.36 (br. dd, $J_{2',4'}$ = 4.3, $J_{4',6'}$ = 1.3 Hz; 1H, 4'-H), 2.85–2.89 (m; 1H, 1'-H), 3.29 (br. dd, $J_{1',2'}$ = 3.6 Hz; 1H, 2'-H), 6.01 (dd, $J_{7',8'}$ = 5.7, $J_{6',7'}$ = 2.7 Hz; 1H, 7'-H), 6.13 (dd, $J_{1',8'}$ = 2.6 Hz; 1H, 8'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.42, 11.67 (two t; C-2, -3), 17.76 (s; C-5'), 34.20 (t; C-9'), 38.75 (d; C-1'), 46.70(d; C-6'), 55.07 (d; C-2'), 57.16 (d; C-4'), 133.84 and 136.75 (two d; C-7', -8'). – MS (70 eV): *m/z* (%) = 149 (3; $M^+ + 1$), 148 (26; M^+), 120(13), 119(16), 106(12), 105(37), 92(44), 91(100), 79(27), 78(18), 77(21), 66(32), 65(22), 41(19), 39(34), 28(13), 27(18).

Spiro[bicyclo[3.2.1]octa-6-ene-2,1'-cyclopropan]-4-one (**4b**): 50 mg (0.340 mmol) of monoepoxide **4a** was submitted to preparative GC using 1.5-m glass column, packed with 10% Apiezon, operated at injector, detector, and column temperatures of 190, 200, and 180°C, respectively, and a carrier gas (N_2) pressure of 1.8 kg/cm². Instead of **4a**, 20 mg (40%) of ketone **4b** was obtained as colorless oil (t_R = 17.5 min). – IR ($CDCl_3$): 3080 cm^{-1}, 3000, 2945, 1730, 1415, 1290, 1270, 1225, 1055, 1035. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.2–0.8 (m; 4H, cyclopropane-H), 1.69 (d, $J_{3x,3n}$ = 17.5 Hz; 1H, 3x-H), 1.94 (br. dd, $J_{1,8a}$ = 5.0, $J_{1,7}$ = 2.8 Hz; 1H, 1-H), 2.19 (d, $J_{8s,8a}$ = 11.3 Hz; 1H, 8s-H), 2.36 (br. ddd, $J_{8a,8s}$ = 11.3, $J_{8a,1}$ = $J_{8a,5}$ = 5.0 Hz; 1H, 8a-H), 2.91 (d, $J_{3n,3x}$ = 17.5 Hz; 1H, 3n-H), 3.07 (br. dd, $J_{5,8a}$ = 5.0, $J_{5,6}$ = 3.0 Hz; 1H, 5-H), 6.02 (br. dd, $J_{6,7}$ = 5.5, $J_{6,5}$ = 3.0 Hz; 1H, 6-H), 6.27 (dd, $J_{7,6}$ = 5.5, $J_{7,1}$ = 2.8 Hz; 1H, 7-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.57 (t), 14.39 (t), 18.31 (s; C-2), 41.21 (t; C-3), 45.21 (t; C-8), 48.70 (d; C-1), 55.40 (d; C-5), 131.72 (d; C-6), 137.65 (d; C-7), 209.71 (s; C=O). – MS (70 eV): *m/z* (%) = 149 (4; $M^+ + 1$), 148 (37, M^+), 105 (39), 92 (46), 91 (100), 79 (24), 66 (34), 65 (20), 39 (34), 28 (21).

$C_{10}H_{12}O$ (148.2) Calcd. C 81.04 H 8.16
Found C 81.00 H 8.45

Spiro[cyclopropane-1,5'-[3,8]dioxatetracyclo[4.3.1.0^{2,4}.0^{7,9}]decane] (**5a**): To a solution of 2.00 g (15.1 mmol) of spiro[bicyclo-[3.2.1]octa-3,6-diene-2,1'-cyclopropane] in 25 ml of absol. CCl_4 was added dropwise while stirring at 0°C (cooling by means of an ice bath) 4.56 g (26.4 mmol) of *m*-CPBA. The hetereogenous mixture was stirred for 6 h at room temp., the solid matter removed by filtration, and the filtrate washed with aqu. Na_2SO_3 (2 × 50 ml), aqu. $NaHCO_3$ (2 × 50 ml), and water (1 × 50 ml) and dried. The solvent was rotoevaporated and the resulting yellow oil was purified by kugelrohr distillation at 110–120°C/0.1 Torr to give 890 mg (36%) of colorless **5a**. An attempt to obtain an analytically pure sample by preparative GC gave the rearranged epoxy ketone **5b**, for which a correct elemental analysis was secured, as given below. – IR (CCl_4): 3060 cm^{-1}, 2980, 2920, 1420, 1385, 1360, 1025, 1000, 950, 915, 895, 840. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.3–0.9 (m; 4H, cyclopropane-H), 1.11 (ddd, $J_{10'a,10's}$ = 11.6, $J_{10'a,1'}$ = 4.8, $J_{10'a,6'}$ = 5.5 Hz; 1H, 10'a-H), 1.33 (br. d, $J_{6',10'a}$ = 5.5 Hz; 1H, 6'-H), 1.66 (br. d, $J_{10's,10'a}$ = 11.6 Hz; 1H, 10's-H), 2.36 (ddd, $J_{4',2'}$ = 4.2, $J_{4',6'}$ = 1.6 Hz; 1H, 4'-H), 2.76 (dd, $J_{1',2'}$ = 4.5, $J_{1',10'a}$ = 4.8 Hz; 1H, 1'-H), 3.2–3.3 (m; 2H, 2'-, 7'-H), 3.52 (d, $J_{9',7'}$ = 3.0 Hz; 1H, 9'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 9.91, 10.89 (two t; C-2, -3), 18.34 (s; C-5'), 19.40 (t; C-10'), 35.17 (d; C-1'), 41.15 (d; C-6'), 53.49 (d), 54.16 (d), 54.24 (d), 56.68 (d). – MS (70 eV): *m/z* (%) = 165 (5; $M^+ + 1$), 164 (39; M^+), 107 (43), 91 (56), 81 (79), 79 (100), 68 (39), 39 (58), 27 (45).

endo-3-Chloro-exo-4-[(2,4-dinitrophenyl)thio]spiro[bicyclo-[3.2.1]octane-6,1'-cyclopropane] (**6a**) *and endo-3-Chloro-exo-2-[(2,4-dinitrophenyl)thio]spiro[bicyclo[3.2.1]octane-6,1'-cyclopropane]* (**6b**): 150 mg (1.12 mmol) of spirocyclopropanes **2a, b** and 263 mg (1.12 mmol) of 2,4-dinitrobenzenesulfenyl chloride in 10 ml of chloroform were stirred at ambient temp. for 15 min. Rotoevaporation of the solvent gave 400 mg of a 1:1 mixture of **6a, b** (HPLC, 400-MHz ^1H NMR), from which **6a** could be separated by flash chromatography [petroleum ether (30–50°C)/ethyl acetate 99:1]. No pure **6b** could be isolated, but the structure could be assessed by comparison of the 400-MHz ^1H-NMR spectra of the mixture **6a, b** with pure **6a**.

6a: ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.50–0.90 (m; 4H, cyclopropane-H), 1.82 (ddd, $J_{7x,7n}$ = 12.0, $J_{7x,1}$ = 7.0, $J_{7x,2x}$ = 1.0 Hz; 1H, 7x-H), 1.80–1.83 (m; 1H, 5-H), 1.88 (ddd, $J_{8s,8a}$ = 12.3, $J_{8s,2n}$ = 2.0, $J_{8s,5}$ = 1.0 Hz; 1H, 8s-H), 1.98 (m; 1H, 8a-H), 2.15 (dddd, $J_{2n,2x}$ = 15.5, $J_{2n,1}$ = 3.5, $J_{2n,3x}$ = 1.5, $J_{2n,8a}$ = 2.0 Hz; 1H, 2n-H), 2.25 (dd, $J_{7n,7x}$ = 12.0, $J_{7n,8s}$ = 2.0 Hz; 1H, 7n-H), 2.43 (dddd, $J_{2x,2n}$ = 15.5, $J_{2x,1}$ = 3.5, $J_{2x,3x}$ = 6.3, $J_{2x,7x}$ = 1.0 Hz; 1H, 2x-H), 2.48–2.53 (m; 1H, 1-H), 3.92 (dd, $J_{4n,5}$ = 2.8, $J_{4n,8a}$ = 1.0 Hz; 1H, 4n-H), 4.28 (br. d, $J_{3x,2x}$ = 6.3 Hz; 1H, 3x-H), 7.63 (d, $J_{6',5'}$ = 9.0 Hz; 1H, 6'-H), 8.47 (dd, $J_{5',6'}$ = 9.0, $J_{5',3'}$ = 2.5 Hz; 1H, 5'-H), 9.08 (d, $J_{3',5'}$ = 2.5 Hz; 1H, 3'-H).

6a, b: IR (CCl_4): 3080 cm^{-1}, 3005, 2950, 2870, 1595, 1530, 1340, 1240, 1050, 920. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 11.76 (t), 12.43 (t), 18.49 (t), 19.34 (t), 23.04 (s), 25.26 (s), 33.14 (t), 33.78 (t), 34.66 (d), 35.81 (t), 37.60 (t), 38.30 (t), 40.45 (d+t), 41.60 (d), 47.43 (d), 52.49 (d), 54.53 (d), 55.80 (d), 55.98 (d), 121.69 (d), 127.68 (d),

144.80 (s), 145.48 (s), 145.52 (s) (aromatic carbons of **6a, b** are not separated). – MS (70 eV): *m/z* (%) = 368 (1, M^+), 133 (91), 105 (56), 91 (100), 79 (77).

6a,b: $C_{16}H_{17}ClN_2O_4S$ (368.8) Calcd. C 52.10 H 4.65 N 7.59
Found C 52.10 H 4.41 N 7.38

Spiro[bicyclo[3.2.1]oct-3-ene-6,2'-[1,3]dioxolane] (**7b**): A mixture of 700 mg (5.73 mmol) of bicyclo[3.2.1]oct-3-en-6-one (**7a**), 40 ml of the 1,3-dioxolane, 40 ml of benzene, and 50 mg of *p*-toluenesulfonic acid was refluxed for 7 h. Excess 1,3-dioxolane and benzene were removed by distillation (120°C/760 Torr, 15-cm Vigreux column). The residue was diluted with 5 ml of benzene, washed with 10 ml of 5% aqu. sodium hydrogencarbonate, and dried with $MgSO_4$. The solution was concentrated under reduced pressure (20°C/20 Torr) and distilled to give 710 mg (72%) of **7b** as a colorless oil, b.p. 54–55°C/1 Torr. – IR (CCl_4): 3030 cm^{-1}, 2940, 2880, 2820, 1640, 1440, 1350, 1300, 1180, 1100, 1020, 960, 680. – ^1H NMR (CCl_4, 90 MHz): δ = 1.4–2.5 (m; 8H), 3.6 (mc; 4H), 5.1–5.6 (m; 2H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.45 (t), 32.96 (t), 36.50 (t), 42.02 (d), 43.06 (d), 63.97 (t), 64.57 (t), 122.57 (s), 125.44 (d), 129.90 (d). – MS (70 eV): *m/z* (%) = 166 (13, M^+), 112 (100), 79 (38).

$C_{10}H_{14}O_2$ (166.2) Calcd. C 72.26 H 8.49
Found C 72.37 H 8.76

endo-3-Chloro-exo-4-[(2,4-dinitrophenyl)thio]bicyclo[3.2.1]-octan-6-one (**8a**)

Method A: 100 mg (0.920 mmol) of **7a** and 216 mg (0.920 mmol) of 2,4-dinitrobenzenesulfenyl chloride in acetonitrile (10 ml) were stirred at ambient temp. for 15 min. After rotoevaporation of the solvent (20°C/20 Torr) the residue was chromatographed (petroleum ether 30–50°C) to give 264 mg (84%) of analytically pure **8a** as yellow needles, m.p. 184–185°C.

Method B: 80.0 mg (0.200 mmol) of **10** and 0.50 ml of 2N H_2SO_4 are refluxed in 50 ml of acetone. After neutralization with solid sodium carbonate, filtration, and rotoevaporation of the solvent (20°C/20 Torr) the residue was diluted with methylene chloride (5 ml), washed with sodium chloride solution (5 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent (20°C/20 Torr) yielded 52.0 mg (73%) of a yellow powder. Recrystallization from ethanol gave pure **8a** as yellow needles, m.p. 184–185°C. – IR ($CDCl_3$): 3100 cm^{-1}, 2960, 1750, 1600, 1530, 1350, 1240, 1160, 1050, 840. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.02 (m; 1H, 8a-H), 2.24 (br. dd, $J_{2n,2x}$ = 15.0, $J_{2n,1}$ = 1.7 Hz; 1H, 2n-H), 2.26 (br. ddd, $J_{8s,8a}$ = 9.5, $J_{8s,7n}$ = 3.5, $J_{8s,4n}$ = 1.0 Hz; 1H, 8s-H), 2.38 (ddd, $J_{7x,7n}$ = 18.5, $J_{7x,1}$ = 7.2, $J_{7x,2x}$ = 1.3 Hz; 1H, 7x-H), 2.68 (dddd, $J_{2x,2n}$ = 15.0, $J_{2x,3x}$ = 5.9, $J_{2x,1}$ = 3.5, $J_{2x,7x}$ = 1.3 Hz; 1H, 2x-H), 2.74 (mc; 1H, 5-H), 2.85 (dd, $J_{7n,7x}$ = 18.5, $J_{7n,8s}$ = 3.5 Hz; 1H, 7n-H), 2.85–2.90 (m; 1H, 1-H), 4.16 (dd, $J_{4n,5}$ = 2.8, $J_{4n,8a}$ = 1.0 Hz; 1H, 4n-H), 4.28 (br. d, $J_{3x,2x}$ = 5.9 Hz; 1-H, 3x-H), 7.59 (d, $J_{6',5'}$ = 9.0 Hz; 1H, 6'-H), 8.49 (dd, $J_{6',5'}$ = 9.0, $J_{5',3'}$ = 2.5 Hz; 1H, 5'-H), 9.09 (d, $J_{3',5'}$ = 2.5 Hz; 1H, 3'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.48 (t), 31.48 (d), 35.99 (t), 43.69 (t), 48.40 (d), 51.82 (d), 53.36 (d), 122.22 (d), 128.02 (d), 128.37 (d), 143.74 (s), 145.04 (s), 146.01 (s), 215.39 (s). – MS (70 eV): *m/z* (%) = 356 (0.2, M^+), 157 (17), 93 (35), 79 (100), 77 (27).

$C_{14}H_{13}ClN_2O_5S$ (356.8) Calcd. C 47.13 H 3.67 N 7.85
Found C 46.89 H 3.86 N 7.92

endo-3-Chloro-exo-4-(phenylthio)bicyclo[3.2.1]octan-6-one (**8b**): 241 mg (1.97 mmol) of **7a** and 295 mg (2.04 mmol) of benzenesulfenyl chloride in 15 ml of chloroform were stirred at ambient temp. for 5 min. After rotoevaporation of the solvent (20°C/20 Torr) the residue was chromatographed to give 381 mg (75%) of a colorless oil, that solidified on cooling to –20°C. Recrystallization from ethanol gave colorless prisms, m.p. 62–64°C. Isomeric products could not be detected (HPLC, 400-MHz ^1H NMR). – IR (CCl_4): 3080 cm^{-1}, 2960, 2920, 2860, 1760, 1580, 1490, 1450, 1270, 1160, 700. – ^1H NMR (C_6D_6, 400 MHz): δ = 1.23 (m; 1H, 8a-H), 1.64 (br. d, $J_{2n,2x}$ = 15.5 Hz; 1H, 2n-H), 1.80 (ddd, $J_{7x,7n}$ = 18.8, $J_{7x,1}$ = 7.1, $J_{7x,2x}$ = 1.3 Hz; 1H, 7x-H), 1.84 (br. ddd, $J_{8s,8a}$ = 12.3, $J_{8s,7n}$ = 3.5, $J_{8s,4n}$ = 1.0 Hz; 1H, 8s-H), 1.94–1.98 (m; 1H, 1-H), 2.13 (dddd, $J_{2x,2n}$ = 15.5, $J_{2x,3x}$ = 5.3, $J_{2x,1}$ = 3.3, $J_{2x,7x}$ = 1.0 Hz; 1H, 2x-H), 2.50 (mc; 1H, 5-H), 2.62 (dd, $J_{7n,7x}$ = 18.8, $J_{7n,8s}$ = 3.9 Hz; 1H, 7n-H), 4.05 (br. s; 1H, 4n-H), 4.09 (br. d, $J_{3x,2x}$ = 5.3 Hz; 1H, 3x-H), 6.90–7.20 (m; 5H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 30.98 (t), 31.84 (d), 34.21 (t), 42.70 (t), 48.06 (d), 53.63 (d), 56.14 (d), 126.96 (d), 128.79 (d), 130.38 (d), 132.76 (s), 215.83 (s). – MS (70 eV): *m/z* (%) = 186 (14), 122 (19), 117 (11), 91 (20), 79 (100).

$C_{14}H_{15}ClOS$ (266.8) Calcd. C 63.00 H 5.70
Found C 62.99 H 5.80

endo-3-Chloro-exo-4-(phenylsulfonyl)bicyclo[3.2.1]octan-6-one (**9**): 30.0 mg (0.112 mmol) of **8b** and 48.3 mg (0.224 mmol) of *m*-chloroperbenzoic acid in methylene chloride (10 ml) were stirred at ambient temp. for 48 h. The mixture was diluted with methylene chloride (5 ml), washed with saturated aqu. sodium hydrogencarbonate (2 × 5 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent (20°C/20 Torr) yielded a yellow residue, which was recrystallized from ethanol to give 27.2 mg (81%) of colorless prisms, m.p. 129–130°C. – IR ($CDCl_3$): 3040 cm^{-1}, 2960, 2930, 2860, 1740, 1460, 1420, 1330, 1160, 820. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.81 (m; 1H, 8a-H), 2.16 (br. d, $J_{2n,2x}$ = 15.0 Hz; 1H, 2n-H), 2.36 (dd, $J_{7x,7n}$ = 18.5, $J_{7x,1}$ = 7.0 Hz, 1H, 7x-H), 2.60–2.82 (m; 5H, 8s-, 2x-, 7n-, 5-, 1-H), 3.63 (br. s; 1H, 4n-H), 4.67 (br. d, $J_{3x,2x}$ = 5.7 Hz; 1-, 3x-H), 7.55–7.85 (m; 5H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.85 (t), 31.16 (d), 37.16 (t), 43.27 (t), 43.93 (d), 49.60 (d), 69.10 (d), 128.70 (d), 129.89 (d), 134.65 (d), 137.92 (s), 215.45 (s). – MS (70 eV): *m/z* (%) = 298 (0.2, M^+), 262 (1), 157 (47), 93 (45), 79 (100).

$C_{14}H_{15}ClO_3S$ (298.8) Calcd. C 56.28 H 5.06
Found C 56.49 H 5.26

endo-3-Chloro-exo-4-[(2,4-dinitrophenyl)thio]spiro[bicyclo-[3.2.1]octane-6,2'-[1,3]dioxolane] (**10**) *and 2-Chloroethyl trans-5-[(2,4-Dinitrophenyl)thio]-3-cyclohexene-1-acetate* (**11**): 200 mg (1.20 mmol) of acetal **7b** and 285 mg (1.22 mmol) of 2,4-dinitrobenzenesulfenyl chloride in 5 ml of acetonitrile were stirred at ambient temp. for 15 min. The precipitate was filtered, washed with 10 ml of petroleum ether (30–50°C), and recrystallized to give 340 mg (71%) of **10** as yellow needles, m.p. 162–163°C (EtOH). – An X-ray analysis (Figure 1, Tables 1 and 2) established the structure. – IR ($CDCl_3$): 3110 cm^{-1}, 2960, 2880, 1600, 1535, 1450, 1250, 1200, 1060, 840. – ^1H-NMR ($CDCl_3$, 400 MHz): δ = AB system (δ_{8s} = 1.80, δ_{8a} = 1.87, $J_{8s,8a}$ = 12.6 Hz; further couplings: $J_{8s,7n}$ = 2.2, $J_{8a,1}$ or $J_{8a,5}$ = 4.4, $J_{8a,1}$ or $J_{8a,5}$ = 4.1 Hz; 2H, 8s-H, 8a-H), 2.03 (ddd, $J_{2n,2x}$ = 15.0, $J_{2n,1}$ = 2.0, $J_{2n,3x}$ = 1.5 Hz; 1H, 2n-H), 2.13 (ddd, $J_{7x,7n}$ = 14.5, $J_{7x,1}$ = 7.5, $J_{7x,2x}$ = 1.3 Hz; 1H, 7x-H), 2.27–2.30 (m; 1H, 1-H), 2.31 (dd, $J_{7n,7x}$ = 14.5, $J_{7n,8s}$ = 2.2 Hz; 1H, 7n-H), 2.41–2.48 (m; 1H, 5-H), 2.57 (dddd, $J_{2x,2n}$ = 15.0, $J_{2x,3x}$ = 4.1, $J_{2x,1}$ = 4.0, $J_{2x,7x}$ = 1.3 Hz; 1H, 2x-H), 3.82–3.86 (m; 1H, OCH_2CH_2O), 4.02–4.10 [m; 4H, OCH_2CH_2O (3H), 4n-H], 4.21 (br. d, $J_{3x,2x}$ = 4.1 Hz; 1H, 3x-H), 7.88 (d, $J_{6',5'}$ = 9.0 Hz; 1H, 6'-H), 8.41 (dd, $J_{5',6'}$ = 9.0, $J_{5',3'}$ = 2.5 Hz; 1H, 5'-H), 9.07 (d, $J_{3',5'}$ = 2.5 Hz; 1H, 3'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.90 (t), 31.04 (d), 39.23 (t), 42.72 (t), 47.96 (d), 49.88 (d), 55.58 (d), 63.97 (t), 65.57 (t), 116.97 (s), 121.76 (d), 127.20 (d), 128.32 (d), 144.25 (s), 145.03 (s), 145.60 (s). – MS (70 eV): *m/z* (%) = 201 (100), 165 (24), 112 (21), 87 (92), 79 (65).

$C_{16}H_{17}ClN_2O_6S$ (400.8) Calcd. C 47.94 H 4.27 N 6.99
Found C 47.98 H 4.24 N 6.67

Chromatography of the mother liquor [petroleum ether (30 to 50°C)/ethyl acetate 8:2] provided besides additional **10** (80 mg; 16%), 15 mg (3%) of yellow needles, m.p. 108–110°C. Spectral and analytical data are consistent with structure **11**. – IR ($CDCl_3$): 3080 cm^{-1}, 3020, 2940, 1740, 1590, 1520, 1340, 1250, 1150, 1050, 860, 830. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.85–2.10 (m; 4H, 2-, 6-H), 2.33–2.44 (m; 2H, $CH_2C=O$), 2.50 (mc; 1H, 1-H), 3.64 (mc; 2H, CH_2Cl), 4.25 (mc; 1H, 5-H), 4.31 (mc; OCH_2), 5.80 (part of AB system, $J_{A,B}$ = 10.0 Hz, further couplings: 5.0, 2.5, 1.5 Hz; 1H, olefinic H), 6.15 (part of AB system, $J_{A,B}$ = 10.0 Hz, further couplings: 5.5, 2.5, 1.5 Hz; 1H, olefinic H), 7.68 (d, $J_{6',5'}$ = 9.0 Hz; 1H, 6'-H), 8.38 (dd, $J_{5',6'}$ = 9.0, $J_{5',3'}$ = 2.5 Hz; 1H, 5'-H), 9.07 (d, $J_{3',5'}$ = 2.5 Hz; 1H, 3'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.98 (d), 31.08 (t), 33.38 (t), 40.15 (t), 41.61 (d), 41.78 (t), 64.02 (t), 121.83 (d), 123.19 (d), 126.96 (d), 127.29 (d), 132.56 (d), 144.01 (s), 145.56 (s), 146.01 (s), 171.46 (s). – MS (70 eV): *m/z* (%) = 321 (4), 201 (23), 121 (35), 93 (42), 79 (100).

$C_{16}H_{17}ClN_2O_6S$ (400.8) Calcd. C 47.94 H 4.27 N 6.99
Found C 47.80 H 4.09 N 7.42

Treatment of Bisepoxide **5a** *with Trifluoroacetic Acid:* To a solution of 120 mg (0.730 mmol) of **5a** in 20 ml of absol. CCl_4 was added at 0°C (ice bath cooling) 83.4 mg (0.730 mmol) of trifluoroacetic acid. After stirring for 15 min, the reaction mixture was washed with aqu. $NaHCO_3$ (2 × 50 ml) and dried. Rotoevaporation of the solvent led to a yellow oil, which was submitted to flash chromatography on silica gel (adsorbent-substrate ratio 50:1), eluting with petroleum ether (30–70°C)/ethyl acetate (6:1). The first eluate consisted of 9 mg (8%) of epoxy ketone **5b** and the second of 100 mg (49%) of hydroxy ester **15**.

Spiro[cyclopropane-1,6'-[3]oxatricyclo[3.3.1.0^{2,4}]nonan]-8'-one (**5b**): IR (CCl_4): 3080 cm^{-1}, 3040, 2950, 2880, 1720, 1600, 1450, 1415, 1375, 1265, 1225, 1020, 845. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.4–0.5 (m; 3H, cyclopropane-H), 0.65–0.71 (m; 1H, cyclopropane-H), 1.59 (br. d, $J_{9'a,9's}$ = 12.0 Hz; 1H, 9's-H), 1.68 (d, $J_{5',9'a}$ = 4.8 Hz; 1H, 5'-H), 1.74 (d, $J_{7'x,7'n}$ = 17.1 Hz; 1H, 7'x-H), 1.80 (dt, $J_{9'a,9's}$ = 12.0, $J_{9'a,5'}$ = $J_{9'a,1'}$ = 5.0 Hz; 1H, 9'a-H), 2.72 (d, $J_{7'n,7'x}$ = 17.1 Hz; 1H, 7'n-H), 3.03 (d, $J_{1',9'a}$ = 5.0 Hz; 1H, 1'-H), 3.51 (d, $J_{4',2'}$ = 2.9 Hz; 1H, 4'-H), 3.62 (d, $J_{2',4'}$ = 2.9 Hz; 1H, 2'-H). – ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 10.64 (t), 13.74 (t), 19.28 (s; C-6'), 26.23 (t; C-7'), 43.73 (d; C-5'), 46.82 (t; C-9'), 51.19 (d; C-1'), 52.76 (d; C-4'), 53.64 (d; C-2'), 208.10 (s; C-8'). – MS (70 eV): *m/z* (%) = 164 (M^+; 27), 121 (21), 107 (33), 93 (37), 91 (71), 81 (68), 79 (100), 77 (55), 68 (32), 53 (36), 39 (53), 27 (35).

$C_{10}H_{12}O_2$ (164.2) Calcd. C 73.15 H 7.37
Found C 72.99 H 7.22

endo-8'-(Trifluoroacetoxy)spiro[cyclopropane-1,6'-exo-[3]oxatricyclo[3.3.1.0^{2,4}]nonan]-exo-7'-ol (**15**): IR (CCl_4): 3600 cm^{-1}, 2920, 1780, 1390, 1220, 1170, 1150, 1025, 955, 940, 910, 895, 840. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.7–0.9 (m; 4H, cyclopropane-H), 1.38 (mc; 1H, 9'a-H), 1.52 (br. d, $J_{5',9'a}$ = 5.0 Hz; 1H, 5'-H), 1.80 (br. d, $J_{9's,9'a}$ = 11.5 Hz; 1H, 9s'-H), 2.64 (br. dd, $J_{1',8'}$ = 3.1, $J_{1',9'a}$ = 5.4 Hz; 1H, 1'-H), 2.17 (mc; 1H, OH), 3.32 (d, $J_{4',2'}$ = 3.1 Hz; 1H, 4'-H), 3.48 (d, $J_{2',4'}$ = 3.1 Hz; 1H, 2'-H), 3.88 (mc; 1H, 8'-H), 4.27 (br. s; 1H, 7'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 9.52 and 13.43 (two t; C-2, -3), 21.22 (t; C-9'), 21.58 (s; C-6'), 40.67 (d), 43.03 (d), 51.95 (d), 53.76 (d), 69.66 (d; C-8'), 85.16 (d; C-7'), 115.0 (q; CF_3), 158.00 (q; C=O). – MS (70 eV): *m/z* (%) = 278 (0.5; M^+), 164 ($M^+ - CF_3CO_2H$; 12), 119 (96), 117 (100), 91 (58), 81 (63), 79 (87), 77 (49), 69 (64), 55 (39), 45 (57), 39 (54), 28 (100).

$C_{12}H_{13}F_3O_4$ (278.2) Calcd. C 51.80 H 4.71
Found C 52.15 H 4.91

Reaction of Oxiranes **3a, b** *with Trifluoroacetic Acid:* To a solution of 600 mg (3.99 mmol) of **3a, b** in 50 ml absol. CCl_4 was added dropwise 454 mg (3.99 mmol) of trifluoroacetic acid while stirring and cooling by means of an ice bath. After stirring for 60 min at room temp., the reaction mixture was washed with aqu. $NaHCO_3$ (2 × 50 ml) and water (1 × 50 ml) and dried. The solvent was rotoevaporated affording 970 mg (97%) of a yellow oil, which was submitted to flash chromatography on silica gel (substrate-adsorbent ratio 100:1), eluting with petroleum ether (30–70°C)/ethyl acetate (10:1). As first fraction eluted 36 mg (6%) of aldehyde **14** as colorless liquid, b. p. 50–60°C/14 Torr. The second fraction consisted of a mixture of three 1,2-*trans* adducts **13a–c**, b. p. 150–160°C/0.1 Torr. The 1,2-*trans* adduct **13d** was obtained as third fraction. The isotwistane **12a** was obtained as main product (278 mg; 26%), b. p. 240–250°C/0.1 Torr, isolated as fourth and final fraction, pure by capillary GC (t_R = 14.49 min) using a 50-m Carbowax glass column, operated at injector, detector, and column temperatures of 190, 200, and 150°C, respectively, and a carrier gas pressure (N_2) of 1.5 kg/cm^2.

3-(Trifluoroacetoxy)tricyclo[4.3.1.0^{3,7}]decan-exo-8-ol (**12a**): IR (CCl_4): 3620 cm^{-1}, 2930, 2830, 1780, 1740, 1450, 1370, 1220, 1170, 1150, 1075, 1035, 995, 860. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (br. d, J = 14.0 Hz; 1H), 1.2–1.4 (m; 2H), 1.68 (br. d, J = 14.0 Hz; 1H), 1.8–2.1 (m; 5H), 2.10 (mc; 1H), 2.18 (br. d, J = 14.0 Hz; 1H), 2.31 (br. s; 1H, OH), 2.3–2.5 (m; 2H), 4.25 (dt, $J_{8,9x}$ = 10.0, $J_{8,7}$ = 3.5 Hz; 1H, 8-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.52 (d), 28.29 (d), 30.11 (t), 34.96 (t), 36.78 (t), 37.69 (t), 42.60 (t), 47.80 (d), 63.35 (d; C-8), 90.04 (s; C-3), 115.0 (q; CF_3), 157.0 (q; C=O). – MS (70 eV): *m/z* (%) = 262 (0.03; M^+), 246 ($M^+ - H_2O$; 0.1), 150 (100), 108 (57), 95 (30), 82 (56), 77 (28), 69 (26), 41 (29), 28 (38).

$C_{12}H_{15}F_3O_3$ (264.2) Cacld. C 54.55 H 5.72
Found C 54.09 H 5.46

Mixture of 1,2-trans Adducts **13a–c**: IR (CCl_4): 3630 cm^{-1}, 3070, 3000, 2940, 2870, 1780, 1450, 1430, 1370, 1220, 1160, 1085, 1010, 970, 950, 920, 880, 855. – ^1H NMR ($CDCl_3$; 400 MHz): δ = 0.3–0.7 (m; 12H, cyclopropane-H), 1.2–2.1 (m; 26H), 2.2–2.6 (m; 3H), 3.4–3.6 (m; 2H), 3.7–3.9 (m; 1H), 4.9–5.1 (m; 1H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.28 (t), 10.73 (t), 11.03 (t), 17.94 (t), 23.35 (s), 23.43 (s), 23.94 (s), 31.65 (t), 31.95 (t), 32.20 (t), 32.39 (t), 32.69 (t), 32.92 (t), 35.88 (t), 35.93 (t), 36.51 (t), 39.72 (d), 39.84 (d), 41.14 (d), 41.97 (d), 42.25 (d), 42.30 (d), 74.58 (d), 75.02 (d), 75.33 (d), 75.43 (d), 78.58 (d), 78.70 (d). – MS (70 eV): *m/z* (%) = 264 (0.17, M^+), 246 ($M^+ - H_2O$; 1), 150 ($M^+ - CF_3CO_2H$; 6), 106 (43), 105 (29), 91 (59), 84 (30), 79 (34), 49 (25), 47 (25), 28 (38).

endo-2-(Trifluoroacetoxy)spiro[bicyclo[3.2.1]octane-6,1'-cyclopropan]-exo-3-ol (**13d**): IR (CCl_4): 3630 cm^{-1}, 3080, 3000, 2940, 2870, 1780, 1450, 1430, 1370, 1340, 1220, 1160, 1080, 1065, 1040, 1030, 1010, 990, 970, 920. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.4–0.7 (m; 4H, 2'-, 3'-H), 1.40 (mc; 1H, 5-H), 1.7–1.8 (m; 4H, 4n-, 7x-, 7n-, 8s-H), 1.95 (br. d, $J_{8a,8s}$ = 11.8 Hz; 1H, 8a-H), 2.03 (ddd, $J_{4x,4n}$ = 15.5, $J_{4x,3}$ = 5.5, $J_{4x,5}$ = 3.0 Hz; 1H, 4x-H), 2.42 (mc; 1H, 1-H), 3.82 (mc; $J_{2,3}$ = 1.2 Hz; 1H, 2-H), 4.92 (br. d, 1H, 3-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.36 and 18.06 (two t; C-2', -3'), 23.24 (s; C-6), 31.34 (t), 31.93 (t), 36.15 (t; C-7), 41.36 (d), 41.91 (d), 73.21 (d), 77.00 (d), 115.0 (q; CF_3), 158 (q; C=O). – MS (70 eV): *m/z* (%) = 264 (1.5; M^+), 150 ($M^+ - CF_3CO_2H$; 23), 121 (15), 117 (48), 107 (30), 106 (85), 95 (40), 93 (66), 91 (100), 77 (54), 69 (49), 41 (47), 39 (35), 28 (19).

$C_{12}H_{15}F_3O_3$ (264.2) Calcd. C 54.55 H 5.72
Found C 54.24 H 5.60

Spiro[2.5]oct-6-ene-4-acetaldehyde (**14**): IR (CCl_4): 3070 cm^{-1}, 3030, 2910, 2840, 2720, 1780, 1730, 1710, 1435, 1220, 1170, 1160, 1010, 660. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.2–0.5 (m; 4H, cyclopropane-H), 1.2–1.9 (m; 3H), 2.3–2.4 (m; 2H), 2.51 (mc; 2H, α-H), 5.66 (mc; 2H, 6-, 7-H), 9.79 (t, $J_{CHO,\alpha}$ = 2.2 Hz; 1H, CHO). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.85 (t), 14.19 (t), 18.95 (s; C-3), 29.69 (t; C-5), 34.95 (d; C-4), 46.03 (t; C-8), 77.31 (t; C-α), 124.89 and 126.53 (two d; C-6, -7), 202.53 (d, CHO). – MS (70 eV): *m/z* (%) = 159 (4; M^+), 106 (40), 91 (100), 79 (82), 78 (71), 77 (48), 67 (36), 41 (39), 39 (42), 27 (29).

$C_{10}H_{14}O$ (150.1) Calcd. C 79.95 H 9.39
Found C 80.18 H 9.61

Tricyclo[4.3.1.0^{3,7}]decane-3,exo-8-diol (**12b**): A solution of 70.0 mg (0.270 mmol) of **12a** and 30.2 mg (0.540 mmol) of KOH in 5 ml of ethanol was allowed to stir at room temp. for 48 h. The yellowish reaction mixture was poured into 10 ml of water and extracted with ethyl acetate (3 × 10 ml). The combined organic layers were dried and after rotoevaporation, 36 mg (80%) of 3,8-diol **12b** was obtained as colorless plates, m. p. 252–253°C (chloroform). An X-ray analysis (Figure 1, Tables 1 and 3) established the structure. – IR (KBr): 3300 cm^{-1}, 2940, 2920, 2860, 1470, 1450, 1300, 1275, 1070, 1045, 1020, 1005, 990. – ^1H NMR ([D_6]DMSO, 400 MHz): δ = 1.0–1.1 (br. d, *J* = 12.5 Hz; 1H), 1.1–1.2 (m; 2H), 1.5–1.9 (m; 9H), 2.2–2.3 (m; 1H), 4.06 (ddd, $J_{8,9x}$ = 10.0, $J_{8,9n}$ = 7.0, $J_{8,7}$ = 4.0 Hz; 1H, 8-H), 4.34 (d, $J_{8\text{-}OH,8}$ = 4.0 Hz; 1H, 8-OH), 4.40 (s; 1H, 3-OH). – ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = 25.53 (d), 29.45 (d), 30.06 (t), 35.76 (t), 38.15 (t), 40.49 (t), 44.98 (t), 49.48 (d), 62.14 (d; C-8), 76.13 (s; C-3). – MS (70 eV): *m/z* (%) = 168 (34, M^+), 150 (26, $M^+ - H_2O$), 108 (31), 95 (100), 79 (40), 77 (28), 55 (44), 41 (37), 39 (26).

$C_{10}H_{16}O_2$ (168.2) Calcd. C 71.39 H 9.59
Found C 71.37 H 9.51

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1a: 109637-49-2 / **1b**: 109637-50-5 / **2a**: 86359-26-4 / **2b**: 86359-25-3 / **3a**: 109637-51-6 / **3b**: 109637-52-7 / **4a**: 109637-53-8 / **4b**: 109637-55-0 / **5a**: 109637-56-1 / **5b**: 109637-57-2 / **6a**: 109637-59-4 / **6b**: 109637-58-3 / **7a**: 31444-32-3 / **7b**: 31444-21-0 / **8a**: 109637-60-7 / **8b**: 109637-62-9 / **9**: 109637-63-0 / **10**: 109637-61-8 / **11**: 109637-64-1 / **12a**: 109637-66-3 / **12b**: 85031-83-0 / **13a**: 109637-67-4 / **13b**: 109637-68-5 / **13c**: 109637-69-6 / **13d**: 109637-70-9 / **14**: 109637-71-0 / **15**: 109637-65-2 / spiro[bicyclo[3.2.1]octa-3,6-diene-2,1′-cyclopropane]: 109637-54-9 / *exo*-2(4),3-dichlorospiro[bicyclo[3.2.1]oct-2(3)-ene-6,1′-cyclopropane]: 109716-81-6

[1] W. Adam, E. Crämer, E. M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **120** (1987) 705.

[2] [2a]G. Olah, G. Ligand, *J. Am. Chem. Soc.* **93** (1971) 6873. – [2b]P. J. Kropp, *J. Am. Chem. Soc.* **91** (1969) 5783. – [2c]A. P. Stoll, H. P. Loosli, P. Niklaus, T. Zardin-Turtaglia, *Helv. Chim. Acta* **61** (1976) 648. – [2d]W. Adam, O. De Lucchi, I. Erden, *J. Am. Chem. Soc.* **102** (1980) 4806. – [2e]W. Adam, O. De Lucchi, *Tetrahedron Lett.* **22** (1981) 3501.

[3] N. Kraus, G. Klein, H. Sadlo, W. Rothenwöhrer, *Synthesis* **1972**, 485.

[4] W. Adam, S. Diaz, A. Rodriguez, *J. Org. Chem.* **43** (1978) 1154.

[5] I. V. Kazimirchik, K. A. Lukin, G. F. Bebikh, N. S. Zefirov, *Zh. Org. Khim.* **19** (1983) 105.

[6] W. Adam, M. Dörr, J. Kron, R. J. Rosenthal, *J. Am. Chem. Soc.*, submitted.

[7] W. Adam, N. Carballeira, E.-M. Peters, K. Peters, H. G. von Schnering, *J. Am. Chem. Soc.* **105** (1983) 5132.

[8] P. A. Carrupt, P. Vogel, *Tetrahedron Lett.* **23** (1982) 2563.

[9] W. Adam, M. Dörr, K. Hill, E.-M. Peters, K. Peters, H. G. von Schnering, *J. Org. Chem.* **50** (1985) 587.

[10] J. Gasteiger, O. Dammer, *Tetrahedron* **34** (1978) 2939.

[11] P. J. De Clerq, *Tetrahedron* **40** (1984) 3729.

[12] M. Kinns, J. K. M. Sanders, *J. Magn. Reson.* **56** (1984) 518.

[13] G. M. Sheldrick, *SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, Universität Göttingen 1983.

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