Transannular Ring Expansion in Electrophilic Reactions of Spirocyclopropane-Substituted Norbornene and Its Oxirane and Azirane Derivatives

Waldemar Adam*[a], Nestor Carballeira[1][a], Elisabeth Crämer[a], Eva-Maria Peters[b], Karl Peters[b], and Hans Georg von Schnering[b]

Institut für Organische Chemie[a], Universität Würzburg, Am Hubland, D-8700 Würzburg (FRG)

Max-Planck-Institut für Festkörperforschung[b], Heisenbergstraße 1, D-7000 Stuttgart 80 (FRG)

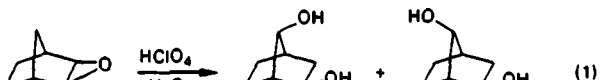
Received October 3, 1986

The spironorbornene **N** gave on treatment with toluenesulfenyl chloride as minor product the 1,2-adduct **N-1a** and as major products the disubstituted brendanes **N-2a,b**. The dispironorbornene **D** gave trace amounts of the 1,2-adduct **D-1a** and essentially exclusively the skeletally rearranged disubstituted brendane **D-2a**. On the other hand, the oxirane **O** led on treatment with trifluoroacetic acid to the hydroxy esters **O-2a,b** which were hydrolyzed to give the respective diols **O-2c,d**, while the azirane **A** afforded the amino esters **A-2a,b**, which were hydrolyzed to yield the respective amino alcohols **A-2c,d**. Neither for the oxirane nor for the azirane were 1,2-adducts observed in these acid-catalyzed reactions. The 2,6-disubstituted brendanes (minor products) were formed via direct transannular ring expansion of the spirocyclopropane moiety in the bridged cations **3** that result from electrophilic attack on the norbornenes. Alternatively, the bridged cations **3** first underwent skeletal rearrangement and subsequent transannular ring expansion led to the 3,8-disubstituted brendanes (major products). X-ray analysis was essential to elucidate rigorously the structures of the sulfones **N-1b** and **N-2c** and the 3,8-diol **O-2d**.

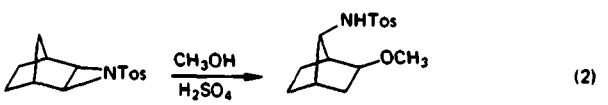
Transannulare Ringerweiterung von Spirocyclopropan-substituierten Norbornenen sowie deren Oxiran- und Aziranderivaten in elektrophilen Reaktionen

Aus dem Spironorbornen **N** entstanden mit Toluolsulfenylchlorid als Nebenprodukt das 1,2-*trans*-Additionsprodukt **N-1a** und als Hauptprodukte die disubstituierten Brendane **N-2a,b**. Das Dispironorbornen **D** lieferte nur Spuren des 1,2-*trans*-Additionsprodukts **D-1a** und fast ausschließlich das umgelagerte, disubstituierte Brendan **D-2a**. Andererseits führte das Oxiran **O** unter Einwirkung von Trifluoressigsäure zu den Hydroxyestern **O-2a,b**, die zu den entsprechenden Diolen **O-2c,d** hydrolysiert wurden. Auch das Aziran **A** lieferte die Aminoester **A-2a,b**, die zu den entsprechenden Aminoalkoholen **A-2c,d** hydrolysiert wurden. Weder in der säurekatalysierten Reaktion des Oxirans noch in der des Azirans konnten 1,2-*trans*-Additionsprodukte beobachtet werden. Die 2,6-disubstituierten Brendane (Nebenprodukte) wurden durch direkte transannulare Ringerweiterung der Spirocyclopropaneinheit im Kation **3** gebildet, das aus elektrophilem Angriff auf die Norbornenderivate resultierte. Die 3,8-disubstituierten Brendane (Hauptprodukte) entstanden durch Gerüstumlagerungen in den Kationen **3** mit nachfolgenden transannularen Ringerweiterungen. Kristallstrukturanalysen der Sulfone **N-1b** und **N-2c** sowie des 3,8-Diols **O-2d** bewiesen zweifellos deren Strukturen.

The norbornyl system has been a favorite target in the elucidation of the intricacies of the Wagner-Meerwein rearrangement[2]. Cases of particular interest here are the acid-catalyzed skeletal rearrangements of norbornene oxide[3] (Eq. 1) and that of the corresponding epimino compound[4] (Eq. 2).



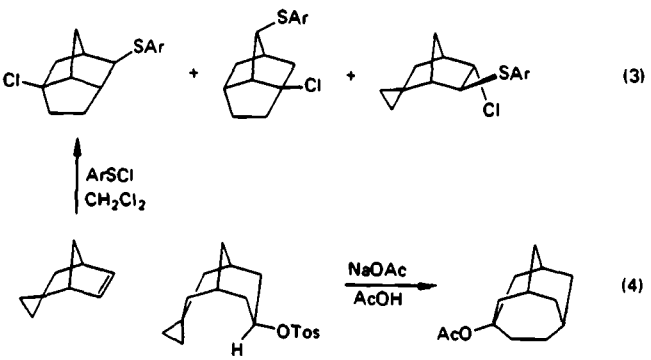
(1)



(2)

Recently we reported[5] that norbornyl cations with remote spirocyclopropane substituents can enter into the novel transannular ring expansion shown in Eq. 3.

In fact, the isomeric brendanes were formed as major products. Only a few other examples of such transannular ring expansions of remote spirocyclopropane moieties are known. For example, an early case[6a] concerns the bicyclo[3.3.1]nonane derivative in Eq. 4. Furthermore, the bicyclo[2.2.2]octane system (Eq. 5) affords the homobrendane derivative via such spirocyclopropane participation[6b]. Finally, more recently, while our work[5] was in progress, another bicyclo[2.2.1]heptane case appeared (Eq. 6), leading in 15% yield to the brendane derivative[6c].

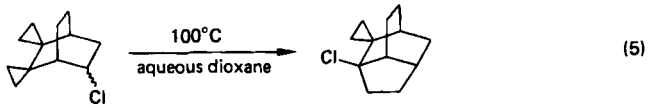


(3) (4)

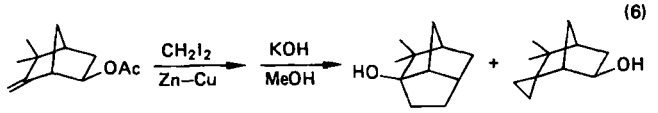
In view of the synthetic potential of such transannular ring expansion of spirocyclopropanes, we examined the acid-catalyzed rearrangements of the oxirane **O** and azirane

  0009–2940/87/0404–0521 $ 02.50/0

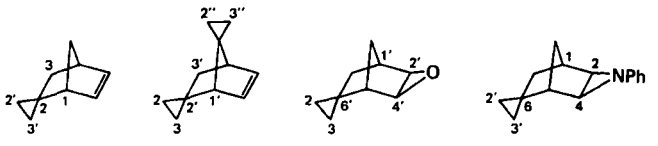
A derived from the norbornene N. Presently we report our findings, together with our previous results[5] on the arenesulfenyl chloride addition to the spironorbornene N and the dispironorbornene D.



(5)



(6)



The previously reported[7] spironorbornene N and dispironorbornene D were readily available by cycloaddition of methylenecyclopropane to cyclopentadiene and spirocyclopropanecyclopentadiene[7a], respectively. The spironorbornene N was epoxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to its oxirane O in 26% yield. The azirane A was obtained in 98% yield via photolysis of the known[8] phenyl azide cycloadduct of the spironorbornene N.

Transformations

The chemistry of the *p*-toluenesulfenyl chloride (ArSCl) addition to the spironorbornene N is summarized in Eq. 7. The normal 1,2-adduct **N-1a** was isolated in ca. 10% yield by kugelrohr distillation. Oxidation with *m*-CPBA afforded the sulfone **N-1b**, whose structure was rigorously established by X-ray analysis (Figure 1, Tables 1, 2).

The isomeric brendanes **N-2a, b** were isolated in 15% and 26%, respectively, by kugelrohr distillation. Reduction of the isomeric brendanes **N-2a, b** with sodium in liquid NH_3 led to the parent brendane **2** (over 90% yield) which was identical to the authentic brendane[9]. Oxidation of the 2,6-isomer **N-2a** with *m*-CPBA afforded the sulfone **N-2c**, whose structure was again rigorously established by X-ray analysis (Figure 1, Tables 1, 3).

Table 1. X-ray operations and results of **N-1b**, **N-2c**, and **O-2d**

Compound	N-1b	N-2c	O-2d
Empirical formula	$C_{16}H_{19}ClSO_2$	$C_{16}H_{19}ClSO_2$	$C_9H_{14}O_2$
Molecular mass [amu]	310.838	310.838	154.211
a [pm] (esd.)	2277.5(6)	1820.8(4)	715.4(2)
b [pm] (esd.)	632.0(2)	745.5(2)	1889.6(6)
c [pm] (esd.)	2294.4(6)	1130.9(3)	637.3(2)
β [deg] (esd.)	111.83(2)	100.95(2)	110.49(3)
Molecular volume [$cm^3 \cdot mol^{-1}$]	230.808	231.146	121.515
No. *Z* of formula units/cell	8	4	4
Calcd. density [$g \cdot cm^{-3}$]	1.347	1.345	1.269
Crystal system	monoclinic	monoclinic	monoclinic
Space group (no.)	*C*2/*c* (15)	$P2_1/c$ (14)	$P2_1/n$ (14)
Crystal size [mm]	0.15 × 1.9 × 0.1	0.45 × 1.0 × 0.2	0.5 × 0.9 × 0.3
No. of measd. intensities	2152	3083	1639
No. of obsd. reflections	2132	2814	1502
No. of structure factors of direct phase determination	418	412	292
R ($\Sigma \mid \Delta F \mid / \Sigma F_o$)	0.039	0.046	0.046
R_w	0.045	0.046	0.049
No. of refd. parameters	181	181	108
Resid. electron density [$e \cdot Å^{-3}$]	0.329	0.281	0.278

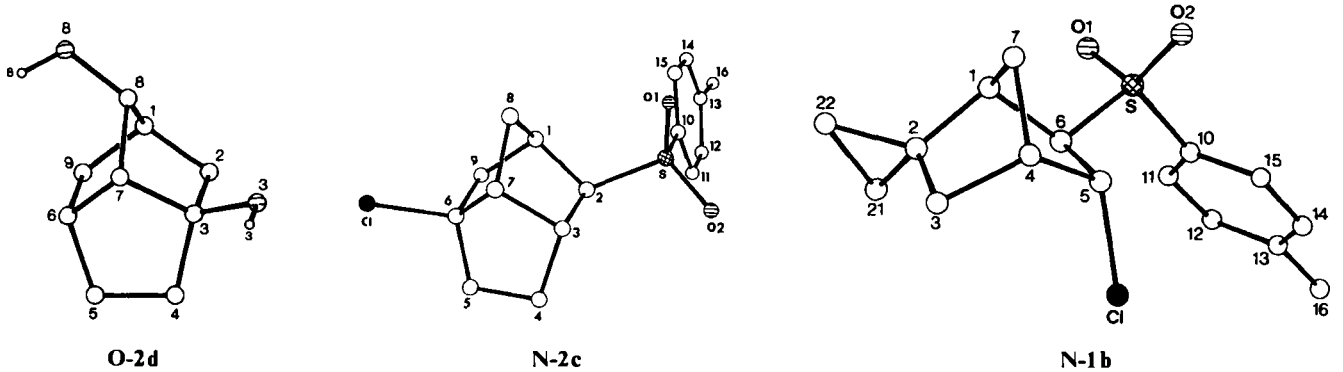


Figure 1. Perspective drawings of the crystal structures of cycloadducts **N-1b**, **N-2c**, and **O-2d**; the numbering of the atoms corresponds to that in Tables 2–4

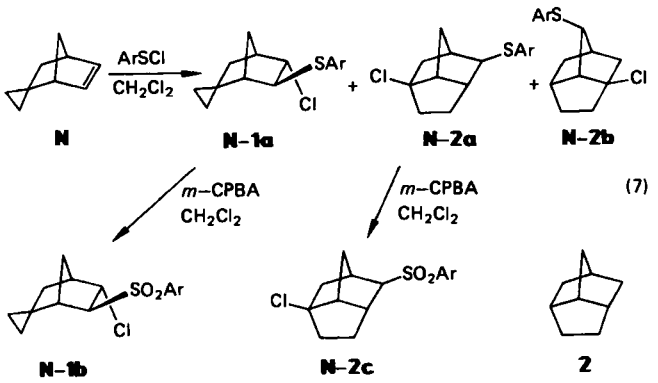
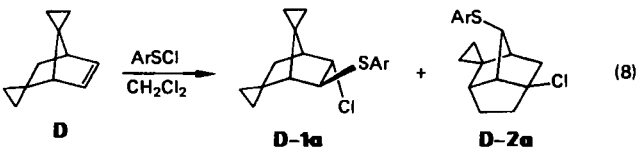


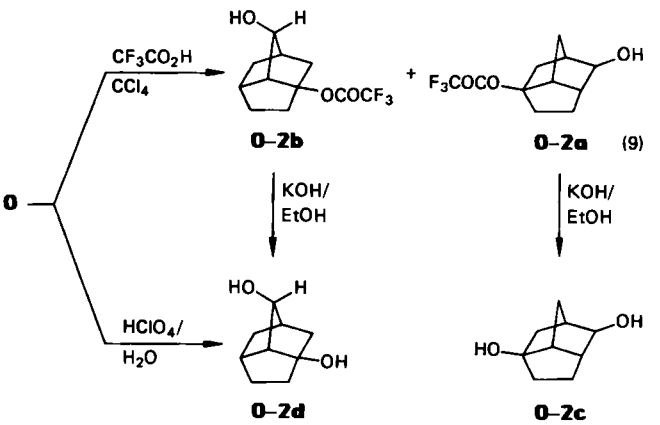
Table 2. Positional [× 10^4] and thermal parameters [$pm^2 \cdot 10^{-1}$] of the atoms of **N-1b**.
Equivalent isotropic U is defined as one third of the trace of the orthogonalised U_{ij} tensor; the standard deviations are given in parentheses

Atom	x	y	z	U(equiv)
S	1415(1)	-527(1)	994(1)	60.1(3)
O(1)	1285(1)	1720(4)	923(1)	68.9(8)
C(1)	739(1)	-939(4)	-284(2)	53(1)
O(2)	1028(1)	-1808(4)	1224(1)	82(1)
C(2)	845(1)	-1172(5)	-896(2)	54(1)
C(3)	907(2)	-3587(5)	-970(2)	64(1)
C(4)	816(2)	-4453(5)	-384(2)	62(1)
C(5)	1384(1)	-3954(4)	205(2)	57(1)
C(6)	1373(1)	-1484(4)	246(1)	50(1)
C(7)	335(2)	-2905(5)	-300(2)	65(1)
C(10)	2211(2)	-852(5)	1495(1)	60(1)
C(11)	2637(2)	784(6)	1556(2)	69(1)
C(12)	3249(2)	582(7)	1970(2)	77(1)
C(13)	3460(2)	-1225(7)	2331(2)	82(2)
C(14)	3032(2)	-2844(7)	2253(2)	85(2)
C(15)	2410(2)	-2696(6)	1843(2)	74(1)
C(16)	4129(2)	-1375(9)	2794(2)	114(2)
C(21)	1214(2)	394(5)	-1100(2)	64(1)
C(22)	513(2)	216(6)	-1445(2)	71(1)
Cl	2122(1)	-4966(1)	207(1)	73.4(3)

The products of the addition of *p*-toluenesulfenyl chloride to the dispironorbornene **D** are given in Eq. 8. Only traces of the 1,2-addition product were obtained, while the skeletally rearranged brendane **D-2a** was isolated in 39% yield by column chromatography on silica gel. No evidence for the transannular ring expansion product without skeletal rearrangement, i.e. the 2,6-disubstituted brendane, could be acquired.

Eq. 9 summarizes the results of the acid-catalyzed reactions with the oxirane **O**. Treatment with trifluoroacetic acid





in CCl_4 gave a ca. 93% yield of the isomeric hydroxy esters **O-2a,b** (in 12:88 relative proportion, respectively, by ^{13}C NMR). Flash chromatography on silica gel resulted in the pure isomers **O-2a** (4%) and **O-2b** (10%), the remaining eluates being mixtures of both. Each pure hydroxy ester was hydrolyzed with KOH in ethanol to give the corresponding diol, respectively, the 2,6-diol **O-2c** (52% yield) and the 3,8-diol **O-2d** (59% yield). The structure of the latter was rigorously established by X-ray analysis (Figure 1, Tables 1, 4).

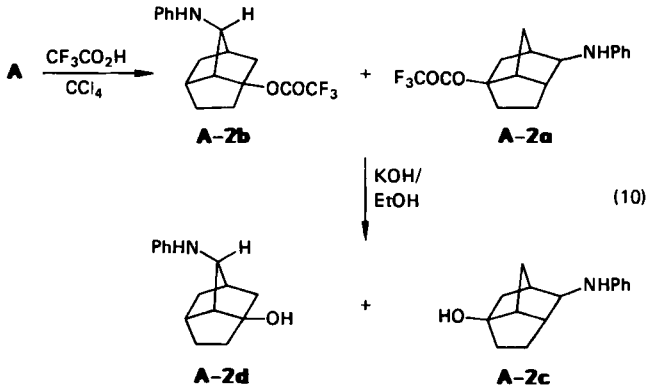
Table 3. Positional [× 10^4] and thermal parameters [$pm^2 \cdot 10^{-1}$] of the atoms of **N-2c**.
U_{eq} as in Table 2, the standard deviations are given in parentheses

Atom	x	y	z	U(equiv)
S	2164(1)	7335(1)	8520(1)	42.8(2)
Cl	4408(1)	3143(1)	903(1)	80.9(4)
O(1)	2229(1)	7897(4)	7331(2)	63.1(8)
O(2)	2328(1)	5499(3)	8851(2)	68.0(9)
C(1)	2633(1)	746(3)	9364(2)	37.8(8)
C(2)	2707(1)	8731(3)	9631(2)	33.6(7)
C(3)	3564(1)	8374(4)	9766(2)	39.3(3)
C(4)	3946(2)	7967(4)	1060(3)	54(1)
C(5)	4098(2)	9808(5)	1671(3)	58(1)
C(6)	3830(1)	1172(4)	689(2)	42.2(8)
C(7)	3856(1)	234(4)	9492(2)	43.4(9)
C(8)	3225(2)	1076(4)	8593(2)	51(1)
C(9)	2993(2)	1694(4)	541(3)	43.4(9)
C(10)	1233(1)	7766(3)	8677(2)	34.3(7)
C(11)	956(1)	6964(4)	9611(2)	42.6(8)
C(12)	214(2)	7242(4)	9693(2)	45.1(9)
C(13)	-256(2)	8278(4)	8870(2)	39.9(9)
C(14)	37(2)	9115(4)	7966(2)	46.3(9)
C(15)	780(2)	8873(4)	7872(2)	42.3(8)
C(16)	-1068(2)	8496(5)	8940(3)	61(1)

With 0.001 N aqueous perchloric acid the oxirane gave in ca. 68% yield a mixture of the isomeric diols **O-2c,d** (in 5:95 relative proportion, respectively, by capillary GC) as a yellow oil. Recrystallization from ethyl acetate afforded the pure 3,8-diol **O-2d** in 51% yield.

Table 4. Positional [× 10^4] and thermal parameters [$pm^2 \cdot 10^{-1}$] of the atoms of **O-2d**.
U_{eq} as in Table 2, the standard deviations are given in parentheses. The U_{eq} for hydrogen atoms represent isotropic thermal parameters

Atom	x	y	z	U(equiv)
C(1)	9146(3)	946(1)	8955(3)	41.7(6)
C(2)	8478(3)	914(1)	989(3)	43.0(6)
O(3)	7333(2)	1954(1)	2352(2)	44.9(5)
C(3)	6816(2)	1482(1)	491(2)	35.9(6)
C(4)	4709(3)	1184(1)	9860(3)	50.0(7)
C(5)	4072(3)	1002(1)	7370(3)	60.5(8)
C(6)	5781(3)	1252(1)	6607(3)	44.7(6)
C(7)	6890(3)	1822(1)	8326(3)	35.7(5)
O(8)	9627(2)	1982(1)	6752(3)	53.2(5)
C(8)	9072(3)	1744(1)	8571(3)	38.8(6)
C(9)	7434(3)	691(1)	6895(3)	50.5(7)
H(3)	6464(34)	2287(13)	2105(37)	83(8)
H(80)	8775(34)	1861(12)	5555(37)	75(7)



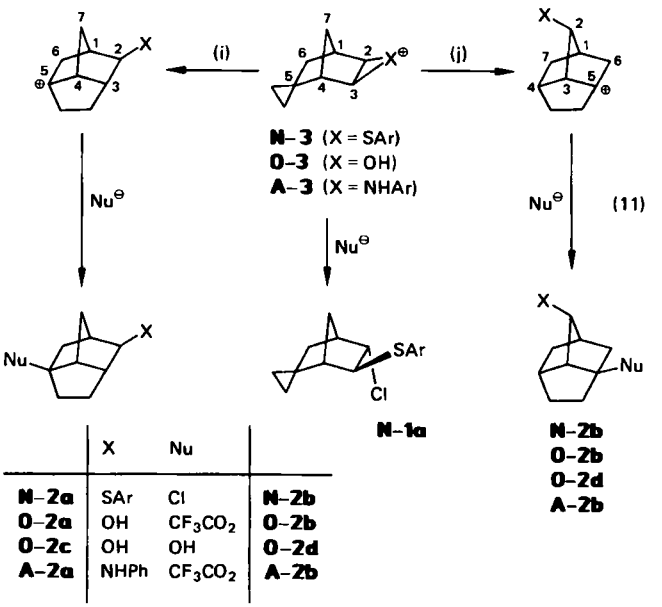
The results of the acid-catalyzed reaction of the azirane **A** are given in Eq. 10. With trifluoroacetic acid in CCl_4 the isomeric amino esters **A-2a,b** (in 1:4 relative proportion, respectively, by capillary GC) were obtained in ca. 69% yield after kugelrohr distillation of the crude reaction product. Flash chromatography on silica gel was not successful in separating the two isomers; however, by means of preparative GC the 3,8-amino ester **A-2b** could be isolated in 95% isomeric purity. Hydrolysis of the mixture of hydroxy esters **A-2a,b** with KOH in ethanol gave the mixture of amino alcohols **A-2c,d** in 54% as a colorless powder. Flash chromatography on silica gel led to the pure hydroxy alcohols, the 2,6-isomer **A-2c** in 11% and the 3,8-isomer **A-2d** in 36% yields, the remaining eluates consisting of mixtures of both isomers.

Structure Assignments

The elucidation of the structures of the disubstituted brendanes **2** was difficult in view of the relatively uninformative ^{1}H-NMR spectra. Except for the protons at the X-substituted carbons, i.e. the 2-H in the 2,6-isomers and the 8-H in the 3,8-isomers (Table 5), the remaining methylenic and methinyl protons caused broad unstructured signals even at 400 MHz. Similarly, also the carbon resonances were difficult to assign, except for the substituted carbons in the 2,6- and the 3,8-series (Table 5). Fortunately, the X-ray structures (Figure 1) of the sulfone **N-2c** in the 2,6-brendane series and the diol **O-2d** in the 3,8-brendane series enabled unequivocal characterization of the disubstituted brendanes. The assigned structures are consistent with the NMR data in Table 5. Additional spectral data are to be found in the Experimental Section under the individual compounds.

Discussion

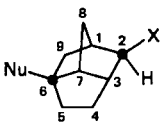
Except for the electrophilic addition of *p*-toluenesulfenyl chloride to spironorbornene **N**, which afforded as minor product the 1,2-adduct **N-1a** with an intact cyclopropane ring, all the acid-catalyzed reactions examined here led to transannular ring expansion of the spirocyclopropane substituent without or with prior skeletal rearrangement (Eq. 11). The observed regioselectivity in the transformation of **N-3** to **N-1a** can be rationalized on steric grounds[10]. In the *exo* configuration of the episulfonium ion **N-3** the *endo* approach of the chloride nucleophile at C-3 is significantly encumbered by steric hindrance of the *syn* hydrogens of the spirocyclopropane moiety at C-5. Thus, *endo* attack at C-2 is preferred leading to the 1,2-adduct **N-1a**.

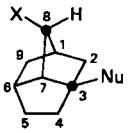


	X	Nu	
N-2a	SAr	Cl	**N-2b**
O-2a	OH	CF_3CO_2	**O-2b**
O-2c	OH	OH	**O-2d**
A-2a	NHPh	CF_3CO_2	**A-2b**

In Eq. 11 the transannular participation of the remote spirocyclopropane substituent is interpreted. Molecular models suggest that ring expansion should be promoted if the incipient *p*-orbital at C-3 in the cationic species **3** points towards the *syn* edge of the spirocyclopropane ring at C-5 due to better overlap with its Walsh orbital. In the bridged cationic species (episulfonium ion **N-3**, protonated oxirane **O-3**, and protonated azirane **A-3**) apparently relatively little cationic charge resides at C-3. In view of the better alignment of the C-4/C-5 σ bond (*anti*-periplanarity), these bridged species **3** prefer first to undergo skeletal rearrangement (path j in Eq. 11) to afford via subsequent transannular

Table 5. Characteristic ^{1}H- and ^{13}C-NMR data of the disubstituted brendanes[a]





X	Nu	Code	2-H[b]	C-2 (d)	C-6 (s)	Code	8-H[b]	C-3 (s)	C-8 (d)
ArS	Cl	**N-2a**[c]	2.59	59.53	73.97	**N-2b**[c]	3.78	73.90	60.27
						D-2a	3.84	73.83	62.70
HO	CF_3CO_2	**O-2a**	3.45	83.35	94.42	**O-2b**	4.30	93.90	79.62
HO	HO	**O-2c**	3.39	84.10	83.43	**O-2d**[d]	4.48	81.44	78.59
PhNH	CF_3CO_2	**A-2a**[e]	2.90	67.00	—[f]	**A-2b**	3.78	93.80	62.66
PhNH	HO	**A-2c**	2.27	66.63	83.86	**A-2d**	3.80	83.24	62.93

[a] Proton resonances are at 400 MHz in $CDCl_3$ unless otherwise stated with $CHCl_3$ as internal standard; carbon resonances are at 100 MHz in $CDCl_3$ unless otherwise stated with $CDCl_3$ as internal standard; all chemical shifts (δ values) pertain to the pure isomers, except when stated. — [b] Broad singlets with no coupling interpretable. — [c] From ref.[5]. — [d] Run in [D_6]DMSO with DMSO as internal standard; the 8-H signal appeared as a pseudo triplet with $J_{8,1} \approx J_{8,7} = 3.0$ Hz; the hydroxy proton resonances appeared at δ = 4.09 and 4.40, respectively, for the 3-OH and 8-OH groups, exchangeable with D_2O. — [e] Measured on the isomer mixture. — [f] This resonance was too weak in the isomer mixture to be detected.

ring expansion and nucleophilic trapping the 3,8-brendanes as the major products. For the dispironorbornene **D** system, from which exclusively the skeletally rearranged, transannularly ring-opened product **D-2a** is obtained (Eq. 8), additional driving force for skeletal rearrangement derives presumably from the formation of a cation prior to transannular ring expansion which is cyclopropylcarbinyl-stabilized by the vicinal spirocyclopropane moiety.

In the rearranged cation resulting from the C-4/C-5 skeletal shift to C-3 (path j), the cationic character at C-4 must necessarily be larger since stabilization by hetero-atom bridging is not possible. In fact, should the C-4 site have assumed full sp^2 hybridization (of course, this is not completely possible in view of the nonclassical nature of norbornyl cations[2]), the 2p orbital at C-4 will be maximally disposed towards overlap with the Walsh orbital of the spirocyclopropane ring, a situation conducive for transannular ring expansion. Competing with this major route (path j in Eq. 11) is direct transannular ring expansion without skeletal rearrangement (path i in Eq. 11), leading after nucleophilic trapping to the 2,6-brendanes as minor products (consult Table 5 for numbering of the brendane products).

We thank the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *Fritz-Thyssen-Stiftung* for financial support of this work. For spectral services we thank Dr. *G. Lange* (MS) and Dr. *D. Scheutzow* (NMR).

Experimental

Boiling and melting points are uncorrected, the latter were taken on a Reichert Thermovar Kofler apparatus. — Infrared (IR) spectra were obtained with 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) instrument, 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) instrument, using $CDCl_3$ as internal standard; the chemical shifts are reported in δ values. — Mass spectra (MS) were measured either with a Varian MAT CH 7 or 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-substrate ratio of at least 20:1. — Analytical gas chromatography was performed on Carlo Erba Strumentazione Model 2900, Fractovap Series, or Model 4100 instruments, equipped with capillary columns and FID. — Preparative gas chromatography employed a Carlo Erba Strumentazione Model 4200. — For analytical HPLC a Kontron liquid chromatograph (Pump 414, UV Detector Uvikon 720 LC, Anacomp Computer) was used, supplied with a LiChrosorb Si 60 (5 mm) column (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 procedure 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 temperature (RT) 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 (ca. 20°C and 15—20 Torr.).

X-ray Crystallograph of **N-1b**, **N-2c**, *and* **O-2d**

The orientation matrix and the cell parameters were determined from transparent colorless crystals of given dimensions on a Syntex-P3 four-circle diffractometer. Measurement of intensities: ω-scan, 1° range, Mo-K_α, 2Θ maximum = 55°. All reflections with $F \geq 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL[11] program system on an Eclipse S/250 was employed. All structures were solved by the direct phase determination. The parameters of the complete structures could be refined by anisotropic least-squares cycles to the given R values. The positions of the hydrogen atoms are calculated geometrically and considered isotropically in all refinements. Special X-ray operations and results of **N-1b**, **N-2c**, and **O-2d** are listed in Table 1, the positional and thermal parameters in Tables 2, 3, and 4. Further

details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (FRG). These data are available with quotation of the registry number CSD 52133, the authors, and the reference to this publication.

General Procedure for the p-Toluenesulfenyl Chloride Additions: A round-bottomed flask was charged with the spiroalkane and equimolar amounts of *p*-toluenesulfenyl chloride in methylene chloride. The reaction mixture was allowed to stir at 20–40°C until completion, as judged by the disappearance of the orange-red color of the sulfenyl chloride. The solvent was roto-evaporated and the crude product purified by repeated column chromatography on silica gel and methylene chloride-pentane as eluant. Final purification for analytical samples was achieved either by distillation or recrystallization. The specific details on the individual systems are summarized below.

Spironorbornene **N**: Following the above general procedure, 1.90 g (15.9 mmol) of spiroalkene **N** was allowed to react with 2.50 g (15.9 mmol) of *p*-toluenesulfenyl chloride in 25 ml of CH_2Cl_2 at ca. 20°C for 30 min, affording on workup the three sulfides **N-1a**, **N-2a**, and **N-2b**. The physical and spectral data are given below.

(endo-5,exo-6)-5-Chloro-6-(p-tolylthio)spiro[bicyclo[2.2.1]heptane-2,1'-cyclopropane] (**N-1a**) was obtained in 10% yield (0.44 g, 1.58 mmol), b.p. 200–210°C at 0.4 Torr, as first eluate in the reaction of spironorbornene **N** with *p*-toluenesulfenyl chloride. – IR (CCl_4): 3080 cm^{-1}, 3025, 2980, 2880, 1500, 1470, 1455, 1430, 1300, 1270, 1240, 1210, 1100, 1020, 940, 875. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.34 (m; 1H), 0.42 (m; 1H), 0.58 (m; 2H), 1.46 (br. s; 1H), 1.56 (ddd, *J* = 12.5, 4.3 and 1.5 Hz; 2H), 1.86 (br. s; 1H), 1.95 (d, *J* = 12.5 Hz; 1H), 2.34 (s; 3H, CH_3), 2.58 (m; 1H, 1-H), 3.39 (dd, *J* = 4.0 and 1.5 Hz; 1H, 6-H), 4.08 (td, *J* = 4.0 and 1.5 Hz; 1H, 5-H), 7.14 and 7.36 (AA'BB'; 4H, C_6H_4). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 9.19 (t), 15.87 (t), 21.05 (q), 25.21 (s), 33.18 (t), 36.67 (t), 46.37 (d), 52.17 (d), 57.99 (d), 66.60 (d), 129.70 (d), 131.48 (d), 136.95 (s).

(endo-5,exo-6)-5-Chloro-6-(p-tolylsulfonyl)spiro[bicyclo[2.2.1]heptane-2,1'-cyclopropane] (**N-1b**) was obtained in 89% yield (24 mg, 0.077 mmol), m.p. 137–138°C (colorless plates from ethanol-carbon tetrachloride), in the reaction of 24 mg (0.086 mmol) of sulfide **N-1a** and 30 mg (0.19 mmol) of *m*-chloroperbenzoic acid in 30 ml of methylene chloride at 20°C for 48 h. – IR (KBr): 3070 cm^{-1}, 3000, 2970, 2940, 2880, 1600, 1500, 1455, 1430, 1410, 1322, 1310, 1290, 1270, 1240, 1160, 1090, 1051, 1030, 1020, 982, 821, 750, 670. – ^1H NMR ($CDCl_3$, 60 MHz): δ = 0.4–0.9 (m; 4H, cyclopropyl), 1.6–2.2 (m; 5H), 2.4 (s; 3H, CH_3), 2.42 (m; 1H, 4-H), 3.20 (dd, *J* = 4.0 and 2 Hz; 1H, 6-H), 4.30 (td, *J* = 4.0 and 2 Hz; 1H, 5-H), 7.10 and 7.52 (AA'BB'; 4H, C_6H_4).

$C_{16}H_{19}ClO_2S$ (310.9) Calcd. C 61.82 H 6.16
Found C 62.05 H 6.24

The X-ray data of **N-1b** are given in Tables 1 and 2 and its structure is exhibited in Figure 1.

(exo-2)-6-Chloro-2-(p-tolylthio)tricyclo[4.2.1.0^{3,7}]nonane (**N-2a**) was obtained in 26% yield (1.15 g, 4.13 mmol), b.p. 150–155°C at 0.1 Torr, as third eluate in the reaction of spironorbornene **N** with *p*-toluenesulfenyl chloride. – IR (CCl_4): 3079 cm^{-1}, 3021, 2980, 2960, 2880, 1500, 1470, 1462, 1453,1450, 1325, 1298, 1270, 1240, 1210, 1100, 1050, 1022, 998, 972, 950. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.50 (m; 2H), 1.78 (d, *J* = 10.5 Hz; 1H), 1.9–2.2 (m; 7H), 2.23 (s; 3H, CH_3), 2.42 (d, *J* = 5 Hz; 1H), 2.59 (br. s; 1H), 6.99 and 7.14 (AA'BB'; 4H, C_6H_4). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.92 (q), 29.35 (t), 34.72 (t), 41.25 (t), 42.04 (d), 46.39 (d), 50.59 (t), 55.63 (d), 59.53 (d), 73.97 (s), 129.64 (d), 131.02 (d), 132.75 (s), 136.42 (s). – MS (70 eV): *m/z* (%) = 278 (39, M^+), 243 (2, $M^+ - Cl$), 155 (60, $C_9H_{12}Cl^+$), 124 (100, $C_7H_8S^+$), 119 (94, $C_9H_{11}^+$), 91 (85, $C_7H_7^+$).

$C_{16}H_{19}ClS$ (278.9) Calcd. C 69.04 H 6.89
Found C 69.18 H 6.87

(exo-2)-6-Chloro-2-(p-tolylsulfonyl)tricyclo[4.2.1.0^{3,7}]nonane (**N-2c**) was obtained in 81% yield (100 mg, 0.32 mmol), m.p. 149–151°C (colorless plates from ethanol), in the reaction of 110 mg (0.40 mmol) of sulfide **N-2a** and 150 mg (0.93 mmol) of *m*-chloroperbenzoic acid in 30 ml of methylene chloride at 20°C for 48 h. – IR (KBr): 3000 cm^{-1}, 2980, 2960, 2940, 2890, 1610, 1500, 1470, 1320, 1310, 1300, 1280, 1155, 1100, 1000, 980, 890, 825, 775, 665. – ^1H NMR ($CDCl_3$, 60 MHz): δ = 1.2–3.0 (m; 12H), 2.40 (s; 3H, CH_3), 7.10 and 7.53 (AA'BB'; 4H, C_6H_4). – MS (70 eV): *m/z* (%) = 310 (0.3, M^+), 157 (39), 155 (100, $C_9H_{12}Cl^+$), 119 (59), 91 (44), $C_7H_7^+$), 79 (19, $C_6H_7^+$), 77 (13, $C_6H_5^+$), 65 (11, $C_5H_5^+$), 41 (11).

$C_{16}H_{19}ClO_2S$ (310.9) Calcd. C 61.82 H 6.16
Found C 61.78 H 6.29

The X-ray data of **N-2c** are given in Tables 1 and 3 and its structure is exhibited in Figure 1.

(anti-8)-3-Chloro-8-(p-tolylthio)tricyclo[4.2.1.0^{3,7}]nonane (**N-2b**) was obtained in 17% yield (75 mg, 2.7 mmol), b.p. 130–135°C at 0.1 Torr, as second eluate in the reaction of spironorbornene **N** with *p*-toluenesulfenyl chloride. – IR (CCl_4): 3080 cm^{-1}, 3020, 2975, 2930, 2880, 1500, 1475, 1458, 1330, 1315, 1298, 1270, 1250, 1185, 1100, 1048, 1024, 1000, 960, 870. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.84 (d, *J* = 12 Hz; 1H), 1.48 (m; 1H), 1.76 (d, *J* = 13.5 Hz; 1H), 1.9–2.6 (m; 8H), 2.30 (s; 3H, CH_3), 3.78 (s; 1H, 8-H), 7.11 and 7.31 (AA'BB'; 4H, C_6H_4). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.90 (q), 29.22 (t), 36.41 (t), 37.42 (d), 41.23 (d), 42.05 (t), 51.64 (t), 56.36 (d), 60.27 (d), 73.90 (s), 129.65 (d), 130.71 (d), 132.78 (s), 136.30 (s). – MS (70 eV): *m/z* (%) = 278 (88, M^+), 243 (9, $M^+ - Cl$), 155 (20, $C_9H_{12}Cl^+$), 124 (90, $C_7H_8S^+$), 119 (95, $C_9H_{11}^+$), 91 (100, $C_7H_7^+$).

$C_{16}H_{19}ClS$ (278.9) Calcd. C 69.04 H 6.89
Found C 69.11 H 6.83

Dispironorbornene **D**: Following the above general procedure, 74 mg (0.51 mmol) of dispiroalkene **D** was allowed to react with 81 mg (0.51 mmol) of *p*-toluenesulfenyl chloride in 5 ml of methylene chloride at ca. 20°C for 30 min, affording the two sulfides **D-1a** and **D-2a**. The physical and spectral data are given below.

(endo-5',exo-6')-5'-Chloro-6'-(p-tolylthio)dispiro[cyclopropane-1,2'-bicyclo[2.2.1]heptane-7',1''-cyclopropane] (**D-1a**) was obtained in traces as first eluate. Only the following spectral data could be obtained due to lack of material. – IR (CCl_4): 3070 cm^{-1}, 2998, 2960, 2925, 2870, 1495, 1452, 1425, 1260, 1020, 945. – ^1H NMR ($CDCl_3$, 60 MHz): δ = 0.2–1.4 (m; 8H, cyclopropyl), 1.7–2.1 (m; 4H, 1'-H, 3'-H_2, 4'-H), 2.30 (s; 3H, CH_3), 3.30 (dd, *J* = 4.0 and 1.5 Hz; 1H, 6'-H), 4.20 (td, *J* = 4.0 and 1.5 Hz; 1H, 5'-H), 6.80 and 7.00 [AA'BB'; 4H, C_6H_4).

(anti-8')-6'-Chloro-8'-(p-tolylthio)spiro[cyclopropane-1,2'-tricyclo[4.2.1.0^{3,7}]nonane] (**D-2a**) was obtained in 39% yield (60 mg, 0.20 mmol), b.p. 190–200°C at 0.10–0.15 Torr, as second eluate. – IR (CCl_4): 3080 cm^{-1}, 3021, 3000, 2980, 2950, 2880, 1500, 1471, 1455, 1320, 1300, 1270, 1220, 1205, 1190, 1100, 1030, 1000, 858. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.25 (ddd, *J* = 9.5, 6, and 5 Hz; 1H, cyclopropyl), 0.40 (ddd, *J* = 9.5, 6, and 5 Hz; 1H, cyclopropyl), 0.56 (ddd, *J* = 9.5, 6, and 5 Hz; 1H, cyclopropyl), 0.92 (ddd, *J* = 9.5, 6, and 5 Hz; 1H, cyclopropyl), 1.50 (m; 2H), 1.84 (m; 1H), 1.96 (d, *J* = 13 Hz; 1H), 2.26 (m; 4H), 2.32 (s; 3H, CH_3), 2.76

(br. d, J = 5 Hz; 1 H), 3.84 (br. s; 1 H, 8'-H), 7.10 and 7.31 (AA'BB'; 4H, C_6H_4). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 4.65 (t), 18.08 (t), 20.96 (q), 26.18 (t), 30.64 (s), 42.46 (t), 44.16 (d), 49.65 (d), 50.36 (t), 55.87 (d), 62.70 (d), 73.83 (s), 129.70 (d), 129.85 (d), 133.73 (s), 135.88 (s). – MS (70 eV): m/z (%) = 304 (30, M^+), 269 (30, $M^+ - Cl$), 181 (12, $C_{11}H_{14}Cl^+$), 180 (16, $C_{11}H_{13}Cl^+$), 145 (100, $C_{11}H_{13}^+$), 144 (27, $C_{11}H_{12}^+$), 137 (20), 129 (17), 124 (73, $C_7H_8S^+$), 117 (29), 115 (19), 105 (64, $C_8H_9^+$), 91 (68, $C_7H_7^+$), 79 (38, $C_6H_7^+$), 77 (34, $C_6H_5^+$), 65 (21, $C_5H_5^+$), 53 (12), 45 (22, CHS^+), 41 (22), 39 (14, $C_3H_3^+$).

$C_{18}H_{21}ClS$ (304.9) Calcd. C 70.91 H 6.94
Found C 70.94 H 6.82

Tricyclo[4.2.1.0^{3,7}]nonane (= Brendane) (**2**): Into a 100-ml three-necked, round-bottomed flask, fitted with a mechanical stirrer, gas inlet, and outlet tubes, was condensed ca. 30 ml of liquid NH_3 at −78°C. To this solution was added in portions while stirring 0.50 g (21.7 mmol) of sodium at −78°C while cooling with a CO_2-acetone bath. Then, 0.30 g (1.08 mmol) of the sulfides **N-2a,b** was added dropwise to the above blue solution. The resulting mixture was stirred under a nitrogen atmosphere for 3 h, warmed to ca. 0°C to evaporate the NH_3, and 5 ml of methanol was added dropwise to destroy the excess sodium. After addition of 5 ml of water and extraction of the aqueous phase with pentane (2 × 5 ml), the combined organic layers were dried with K_2CO_3. Pentane was distilled off (ca. 36°C at 760 Torr), affording 120 mg (91% yield) of a waxy solid, m.p. 98–99°C (ref.[9] m.p. 98–99°C). – IR (CCl_4): 2960 cm^{-1}, 2880, 1460, 1340, 1321, 1300. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 0.70 (s; 1 H), 0.87 (s; 1 H), 1.38–2.33 (m; 12 H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 32.23 (t), 35.81 (d), 39.11 (t), 39.97 (d), 40.97 (t), 48.13 (d).

Spiro[cyclopropane-1,6'-[3]oxatricyclo[3.2.1.0^{2,4}]octane] (**O**): To a solution of 3.00 g (25.0 mmol) of spirocyclopropanenorbornene **N** in 50 ml of dry methylene chloride was added ca. 200 mg of $NaHCO_3$. While stirring, at 0°C was added to the suspension in portions ca. 5.95 g (35.0 mmol) of *m*-chloroperbenzoic acid, and the suspension was allowed to stir at ca. 20°C for 24 h. After removal of the solid by filtration, the filtrate was washed with aqueous Na_2SO_3 (2 × 20 ml), 2 N NaOH (2 × 20 ml), and H_2O (2 × 20 ml) and dried with $MgSO_4$. The solvent was roto-evaporated at water aspirator pressure (ca. 20°C at 20 Torr) yielding 2.90 g (85%) of yellow oil as crude product, which was purified by kugelrohr distillation (80–89°C at 0.1 Torr), affording 970 mg (26%) of a colorless, wax-like product. – IR (CCl_4): 3040 cm^{-1}, 3020, 3000, 2980, 2875, 1375, 1280, 1040, 1025, 965, 860. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 0.1–0.7 (m; 4H, 2-H, 3-H), 1.0–1.6 (m; 4H, 7'-H, 8'-H), 1.6–1.8 (m; 1 H, 5'-H), 2.4–2.6 (m; 1 H, 1'-H), 3.0–3.3 (m; 2H, 2'-H, 4'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.00 and 11.80 (two t; C-2, C-3), 23.26 (s; C-6'), 27.16 (t; C-8'), 36.62 (t; C-7'), 38.71 (d; C-1'), 45.20 (d; C-5'), 50.81 and 51.65 (two d; C-2', C-4'). – MS (70 eV): m/z (%) = 136 (6, M^+), 91 (55), 80 (42), 79 (100), 77 (49), 39 (49), 28 (60).

$C_9H_{12}O$ (136.2) Calcd. C 79.37 H 8.88
Found C 79.32 H 8.95

3-Phenylspiro[[3]azatricyclo[3.2.1.0^{2,4}]octane-6,1'-cyclopropane] (**A**): A solution of 810 mg (3.40 mmol) of phenyl azide cycloadduct[8] of spironorbornene **N** in 10 ml of dry benzene was irradiated at 300 nm in the Rayonet Photochemical Reactor (Model PR 100) until complete conversion (ca. 50 min), as monitored by ^1H NMR. After roto-evaporation of the solvent (ca. 40°C at 20 Torr) and distillation of the crude product, there was obtained 700 mg (98%) of azirane **A** as colorless oil, b.p. 215–220°C at 0.1 Torr. – IR (CCl_4): 3070 cm^{-1}, 3030, 3000, 2960, 2860, 1595, 1490, 1365, 1285, 1260, 1070, 1030, 865. – ^1H NMR ($CDCl_3$; 400 MHz; n = *endo*, x = *exo*, a = *anti*, s = *syn*): δ = 0.2–0.6 (m; 4H, 2'-H, 3'-H), 1.18 (d, $J_{7n,7x}$ = 11.5 Hz; 1 H, 7n-H), 1.28 (br. d, $J_{8a,8s}$ = 9.5 Hz; 1 H, 8a-H), 1.54 (br. d, $J_{7x,7n}$ = 11.5 Hz, $J_{7x,1}$ = 3.8 Hz; 1 H, 7x-H), 1.66 (br. d, $J_{8s,8a}$ = 9.5 Hz; 1 H, 8s-H), 2.33 (d, $J_{4,2}$ = 5.5 Hz; 1 H, 4-H), 2.44 (d, $J_{2,4}$ = 5.5 Hz; 1 H, 2-H), 2.59 (br. s; 1 H, 1-H), 1.74 (br. s; 1 H, 5-H), 6.8–7.0 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.27 and 12.73 (two t; C-2', C-3'), 24.16 (s; C-6), 29.99 (t; C-8), 38.12 (t; C-7), 38.50 (d; C-1), 40.40 (d; C-5), 41.45 and 45.10 (two d; C-2, C-4), 120.86 (d), 121.37 (d), 128.78 (d), 153.32 (s; phenyl C-1). – MS (70 eV): m/z (%) = 211 (46, M^+), 183 (31), 156 (63), 131 (80), 130 (65), 119 (39), 104 (49), 91 (37), 77 (100), 51 (29).

$C_{15}H_{17}N$ (211.3) Calcd. C 85.26 H 8.11 N 6.63
Found C 85.17 H 8.17 N 6.76

General Procedure for the Trifluoroacetic Acid-Catalyzed Reactions: The substrate (1.0–3.0 mmol) was dissolved in 30 ml of dry CCl_4, and equimolar amounts of trifluoroacetic acid was added at ca. 0°C while stirring. After stirring at 0°C for additional 5–10 min, the reaction mixture was poured into 30 ml of H_2O and extracted with CH_2Cl_2 (3 × 15 ml). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (1 × 50 ml), dried with $MgSO_4$, and the solvent was removed by roto-evaporation (ca. 20°C at 20 Torr). The yellow-brown product was purified by distillation and/or chromatography as described for the individual cases below.

Oxirane **O**: According to the above general procedure, from 641 mg (4.71 mmol) of oxirane **O** and 537 mg (4.71 mmol) of trifluoroacetic acid in 30 ml of dry CCl_4 was obtained 1.10 g (93%) of a yellow oil. Silica gel chromatography (1:50 ratio of substrate to adsorbent with 6:1 petroleum ether (30–70)/ethyl acetate as eluant) gave two fractions, the first containing pure hydroxy ester **O-2b**, 120 mg (10%) of colorless oil, b.p. 110–120°C at 0.5 Torr, the second containing the pure hydroxy ester **O-2a**, 46 mg (4%) of colorless wax, b.p. 120–125°C at 0.5 Torr.

(anti-8)-3-(Trifluoroacetoxy)tricyclo[4.2.1.0^{3,7}]nonan-8-ol (**O-2b**): IR (CCl_4): 3620 cm^{-1}, 3600–3200, 2970, 2880, 1780, 1370, 1220, 1170, 1080, 1050, 1000, 970, 925, 870. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.94 (br. dd, J = 12.4 Hz, J' = 2.0 Hz; 1 H), 1.57 (mc; 1 H), 1.82–2.12 (m; 6H), 2.28 (mc; 1 H), 2.39–2.58 (m; 3H), 4.30 (br. s; 1 H, 8-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.52 (t), 34.76 (t), 35.68 (d), 36.22 (t), 40.44 (d), 45.14 (t), 55.48 (d; C-7), 79.62 (d; C-8), 93.90 (s; C-3), 116.60 (q; CF_3), 157.20 (q; C=O). – MS (70 eV) of mixture **O-2a,b**: m/z (%) = 250 (0.3, M^+), 136 (100), 108 (46), 95 (71), 92 (80), 80 (58), 79 (85), 69 (62), 55 (45), 41 (65).

$C_{11}H_{13}F_3O_3$ (250.2) Calcd. C 52.80 H 5.24
(mixture **O-2a,b**) Found C 52.84 H 5.42

(exo-2)-6-(Trifluoroacetoxy)tricyclo[4.2.1.0^{3,7}]nonan-2-ol (**O-2a**): IR (CCl_4): 3615 cm^{-1}, 3600–3200, 2960, 2880, 1780, 1370, 1220, 1170, 1085, 1065, 1020, 980, 875. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.58–1.69 (m; 4H), 1.80–2.21 (m; 6H), 2.44 (ddd, J = 13.0 Hz, J' = 9.5 Hz, J'' = 3.5 Hz; 1 H), 2.60 (br. d, J = 5.0 Hz; 1 H), 3.45 (br. s; 1 H, 2-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.12 (t), 33.74 (t), 34.74 (t), 42.17 (t), 43.72 (d), 47.90 (d), 49.87 (d), 83.35 (d; C-2), 94.42 (s; C-6), 114.0 (q; CF_3), 156.80 (q; C=O).

MS and CH analyses were determined for the isomeric mixture **O-2a,b** and are given under isomer **O-2b**.

Azirane **A**: According to the above general procedure, from 260 mg (1.23 mmol) of azirane **A** and 140 mg (1.23 mmol) of trifluoroacetic acid in 30 ml of dry CCl_4 was obtained 276 mg (69%) of a yellow oil, b.p. 230–240°C at 0.1 Torr, which by capillary GC (40-m OV-101 capillary column, operated at a column temperature

of 180°C and a nitrogen carrier gas pressure of 1.0 kg/cm^2) consisted of a 1:4 mixture of **A-2a,b**, respectively. By means of preparative gas chromatography (1.5-m glass column, packed with 10% Apiezon L and operated at injector, column, and detector temperatures of 200, 170 and 225°C, respectively, and a nitrogen carrier gas pressure of 2.0 kg/cm^2) the major isomer **A-2b** could be obtained in ca. 95% isomeric purity.

(anti-8)-8-Phenylamino-3-(trifluoroacetoxy)tricyclo[4.2.1.0^{3,7}]nonane (**A-2b**): IR of mixture **A-2a,b** (CCl_4): 3410 cm^{-1}, 3040, 2950, 2835, 1785, 1605, 1505, 1372, 1320, 1225, 1170, 1155, 910. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.96 (br. d, J = 12.6 Hz; 1H), 1.55–1.65 (m; 1H), 1.95–2.21 (m; 5H), 2.33 (mc; 1H), 2.47–2.55 (m; 2H), 2.62–2.66 (m; 1H), 3.0–3.5 (br. s; 1H, N-H), 3.78 (s; 1H, 8-H), 6.60–6.75 (m; 3H, *meta*- and *para*-H), 7.15–7.21 (m; 2H, *ortho*-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.33 (t), 34.98 (d), 35.62 (t), 35.83 (t), 38.44 (d), 46.26 (t), 54.35 (d), 62.66 (d; C-8), 93.80 (s; C-3), 112.92 (d), 114.50 (q; CF_3), 117.65 (d), 129.27 (d), 147.58 (s; C-1″), 156.60 (q; C=O). – MS (70 eV) of mixture **A-2a,b**: m/z (%) = 325 (100; M$^+$), 183 (35), 132 (42), 119 (46), 106 (55), 93 (48), 77 (48), 49 (45).

$C_{17}H_{18}F_3NO_2$ (325.3) Calcd. C 62.67 H 5.58 N 4.31
(mixture **A-2a,b**) Found C 63.01 H 5.48 N 4.07

(exo-2)-2-Phenylamino-6-(trifluoroacetoxy)tricyclo[4.2.1.0^{3,7}]nonane (**A-2a**)

^{1}H NMR of mixture **A-2a,b** ($CDCl_3$, 400 MHz): δ = 1.7–2.4 (m; 11H), 2.90 (br. s; 1H, 2-H), 3.46–3.88 (br. s; 1H, N–H), 7.2–6.8 (m; 5H, phenyl-H). – ^{13}C NMR of mixture **A-2a,b** ($CDCl_3$, 100 MHz): δ = 26.92, 34.45, 34.55, 40.72, 44.37, 45.44, 50.24, 67.00 (d; C-2); the remaining resonances could not be detected due to superposition with the **A-2b** isomer in the mixture.

MS and CHN analyses are given under isomer **A-2b**.

(anti-8)-Tricyclo[4.2.1.0^{3,7}]nonane-3,8-diol (**O-2d**). – a) *Perchloric Acid-Catalyzed Reaction of Oxirane* **O**: A suspension of 1.00 g (7.34 mmol) of oxirane **O** in 5 ml of ca. 0.001 N aqueous $HClO_4$ was vigorously stirred at ca. 60°C for 20 min. The colorless reaction mixture was neutralized with ca. 0.2 N NaOH, extracted with ethyl ether (3 × 30 ml), and the combined organic phases were dried with $MgSO_4$. After roto-evaporation of the solvent at water aspirator pressure (ca. 20°C at 20 Torr), a yellow oil was obtained which on recrystallization from ethyl acetate gave 574 mg (51%) of colorless prisms, m.p. 254–255°C. – IR (KBr): 3600–3100 cm^{-1}, 2960, 2865, 1465, 1320, 1240, 1203, 1120, 1030. – ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 0.69 (d, J = 11.4 Hz; 1H), 1.25 (d, J = 12.5 Hz; 1H), 1.30 (mc; 1H), 1.6–1.9 (m; 6H), 2.0–2.2 (m; 1H), 2.2–2.3 (m; 1H), 4.09 (br. s; 1H, 3-OH), 4.40 (br. s; 1H, 8-OH), 4.48 (br. d, J = 3.0 Hz, 1H, 8-H). – ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 28.30 (t), 35.40 (t), 36.76 (t), 39.70 (d), 40.15 (d), 46.72 (t), 56.58 (d; C-7), 78.59 (d; C-8), 81.44 (s; C-3). – MS (70 eV): m/z (%) = 154 (3, M$^+$), 136 (91, M$^+$ – H_2O), 95 (82), 83 (100), 81 (76), 55 (59), 41 (51).

$C_9H_{14}O_2$ (154.2) Calcd. C 70.10 H 9.15
Found C 70.43 H 9.47

b) *Hydrolysis of Hydroxy Ester* **O-2b**: A sample of 533 mg (2.13 mmol) of hydroxy ester **O-2b** and 250 mg of KOH were taken up in 2 ml of H_2O and 10 ml of ethanol. Then the reaction mixture was stirred at ca. 20°C for 48 h, poured into ca. 50 ml of H_2O, and extracted with ethyl acetate (3 × 30 ml). The combined organic phases were dried with $MgSO_4$ and the solvent roto-evaporated at water aspirator pressure (ca. 40°C at 20 Torr), yielding 193 mg (59%) of colorless prisms of **O-2d**, m.p. 254–255°C (ethyl acetate). This product was identical to that obtained above in the $HClO_4$-catalyzed reaction.

The X-ray data of **O-2d** are given in Tables 1 and 4 and its structure is exhibited in Figure 1.

(exo-2)-Tricyclo[4.2.1.0^{3,7}]nonane-2,6-diol (**O-2c**): Following the procedure for the **O-2b** to **O-2d** transformation, from 171 mg (0.68 mmol) of hydroxy ester **O-2a** and 77 mg KOH in 1 ml of H_2O and 5 ml of ethanol was obtained 55.0 mg (52%) of colorless powder of the 2,6-diol **O-2c**. Recrystallization from 1:1 petroleum ether (30–70)/ethyl acetate afforded 55 mg (52%) of colorless needles, m.p. 232–233°C. – IR ($CDCl_3$): 3610 cm^{-1}, 3600–3300, 2960, 2880, 1460, 1440, 1315, 1085, 1030, 1015, 860. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.2–1.3 (m; 2H), 1.44–2.14 (m; 11H), 3.39 (s; 1H, 2-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.74 (t), 33.45 (t), 38.63 (t), 43.51 (t), 43.60 (d), 49.00 (d), 51.13 (d), 83.43 (s; C-6), 84.10 (d; C-2). – MS (70 eV): m/z (%) = 154 (43, M$^+$), 136 (20; M$^+$ – H_2O), 97 (49), 96 (92), 84 (62), 83 (100), 79 (40), 67 (23), 57 (25), 55 (50), 43 (38), 41 (36), 39 (25).

$C_9H_{14}O_2$ (154.2) Calcd. C 70.10 H 9.15
Found C 69.81 H 9.17

Amino Alcohols **A-2c,d** *via Hydrolysis of Amino Esters* **A-2a,b**: Following the above procedure for the saponification of **O-2b** to **O-2d**, from 550 mg (1.69 mmol) of the mixture of amino esters **A-2a,b** and 189 mg of KOH in 2 ml of H_2O and 10 ml of ethanol at ca. 20°C for 48 h was obtained 209 mg (54%) of the isomeric amino alcohols **A-2c,d** as colorless powder. The isomers were separated by flash chromatography on silica gel (50:1 adsorbent-substrate ratio, eluting with 1:1 petroleum ether (30–70)/ethyl acetate). The first eluate contained 139 mg (36%) of the pure isomer **A-2d** as colorless powder, m.p. 158–160°C (ethyl acetate) and the second eluate 41.0 mg (11%) of colorless powder of pure isomer **A-2c**, m.p. 118–119°C (ethyl acetate).

(anti-8)-8-Phenylaminotricyclo[4.2.1.0^{3,7}]nonan-3-ol (**A-2d**): IR (CCl_4): 3610 cm^{-1}, 3600–3300, 3430, 3060, 3030, 2960, 2880, 1605, 1505, 1430, 1315. – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 8.89 (br. d, J = 12.5 Hz; 1H), 1.4–1.5 (m; 1H), 1.59 (d, J = 13.0 Hz; 1H), 1.8–2.2 (m; 8H), 2.28 (mc; 1H), 2.4–2.5 (m; 1H), 3.80 (br. s; 1H, 8-H), 6.6–7.2 (m; 5H, phenyl-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.38 (t), 35.95 (d), 36.73 (t), 38.43 (d), 39.66 (t), 47.91 (t), 55.97 (d), 62.93 (d; C-8), 83.24 (s; C-3), 113.10 (d), 117.37 (d), 129.20 (d), 147.76 (s). – MS (70 eV): m/z (%) = 229 (64, M$^+$), 146 (16), 106 (24), 93 (100), 77 (18).

$C_{15}H_{19}NO$ (229.3) Calcd. C 78.56 H 8.35 N 6.11
Found C 78.35 H 8.28 N 6.12

(exo-2)-2-Phenylaminotricyclo[4.2.1.0^{3,7}]nonan-6-ol (**A-2c**): IR ($CDCl_3$): 3610 cm^{-1}, 3600–3300, 3430, 2960, 2870, 1600, 1500, 1320, 1150, 1020, 870. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.49 (dd, J = 13.0 Hz, J = 2.1 Hz; 1H), 1.63–1.96 (m; 7H), 2.00–2.18 (m; 4H), 2.27 (br. d, J = 3.8 Hz; 1H, 2-H), 3.5–3.9 (br. s; 1H, N–H), 6.5–6.8 (m, 3H, phenyl-H), 7.1–7.4 (m; 2H, phenyl-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.80 (t), 34.44 (t), 38.66 (t), 41.30 (d), 45.94 (t), 47.07 (d), 51.70 (d), 66.63 (d; C-2), 83.86 (s; C-6), 113.18 (d), 117.07 (d), 129.23 (d), 147.00 (s). – MS (70 eV): m/z (%) = 229 (52, M$^+$), 146 (27), 132 (59), 106 (100), 93 (28), 77 (26), 28 (20), 18 (21).

$C_{15}H_{19}NO$ (229.3) Calcd. C 78.56 H 8.35 N 6.11
Found C 78.46 H 8.42 N 5.90

CAS Registry Numbers

2: 1521-75-1 / **A**: 106435-07-8 / **A-2a**: 106435-12-5 / **A-2b**: 106435-11-4 / **A-2c**: 106435-14-7 / **A-2d**: 106435-13-6 / **D**: 94348-06-8 /

D-1a: 106455-76-9 / **D-2a**: 106435-05-6 / **N**: 6572-50-5 / **N** phenylazide cycloadduct: 106435-15-8 / **N-1a**: 86146-95-4 / **N-1b**: 106435-04-5 / **N-2a**: 86146-93-2 / **N-2b**: 86146-94-3 / **N-2c**: 86146-98-7 / **O**: 106435-06-7 / **O-2a**: 106435-08-9 / **O-2b**: 106455-77-0 / **O-2c**: 106435-10-3 / **O-2d**: 106435-09-0 / *p*-toluenesulfenylchloride: 933-00-6 / trifluoroacetic acid: 76-05-1 / perchloric acid: 7601-90-3

[1] Present address: Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931, USA; a travel grant from the *Fritz-Thyssen-Stiftung* is gratefully acknowledged.

[2] [2a] C. A. Grob, *Acc. Chem. Res.* **16** (1983) 426; C. A. Grob, *Angew. Chem.* **94** (1982) 87; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 87. – [2b] H. C. Brown, *Acc. Chem. Res.* **16** (1983) 432. – [2c] G. A. Olah, G. K. Surya Prakash, M. Saunders, *Acc. Chem. Res.* **16** (1983) 440. – [2d] C. Walling, *Acc. Chem. Res.* **16** (1983) 448.

[3] H. Christol, J. Coste, F. Pietrasanta, F. Plénat, G. Renard, *J. Chem. Res.* (*S*) **1978**, 62.

[4] R. Huisgen, L. Möbius, G. Müller, H. Stangl, G. Szeimies, J. M. Vernon, *Chem. Ber.* **98** (1965) 3992.

[5] [5a] W. Adam, N. Carballeira, E.-M. Peters, K. Peters, H. G. von Schnering, *J. Am. Chem. Soc.* **105** (1983) 5132. – [5b] W. Adam, E. Crämer, *Tetrahedron Lett.* **27**, 3361 (1986).

[6] [6a] M. A. Eakin, J. C. Martin, W. Parker, *J. Chem. Soc., Chem. Commun.* **1967**, 955. – [6b] A. de Meijere, O. Schallner, C. Weitemeyer, W. Spielmann, *Chem. Ber.* **112** (1979) 908. – [6c] R. Krishna, H. P. Chawla, S. Dev, *Indian J. Chem.* **22** (1983) 193.

[7] [7a] W. Adam, M. Dörr, K. Hill, E.-M. Peters, K. Peters, H. G. von Schnering, *J. Org. Chem.* **50** (1985) 587. – [7b] I. V. Kazimirchik, K. A. Lukin, G. F. Bebikh, N. S. Zefirov, *Zh. Org. Khim.* **19** (1983) 105.

[8] W. Adam, N. Carballeira, E. Crämer, V. Lucchini, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.*, in press.

[9] A. Nickon, H. R. Kwasnik, C. T. Mathew, T. D. Swartz, R. O. Williams, J. B. Di Giorgio, *J. Org. Chem.* **43** (1978) 3904.

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

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

[238/86]