109. The Intramolecular *Ramberg-Bäcklund* Reaction: A Convenient Method for the Synthesis of Strained Bridgehead Olefins[1])

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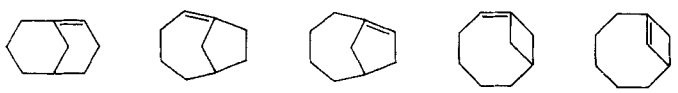
Summary

The stereochemical aspects of the intramolecular *Ramberg-Bäcklund* reaction, *i.e.* the 1,3-elimination of hydrogen halide followed by sulfur dioxide extrusion, have been studied on the α-bromosulfones of the 1-thiadecalin[3]) series. Whereas the *cis, exo*-bromosulfone **23a** containing the ideal W-type arrangement of the reacting atoms undergoes a clean *Ramberg-Bäcklund* reaction, the *trans, exo-* and *trans, endo*-bromosulfones, **24a** and **24b**, respectively, lead to an α,β-unsaturated sulfone by simple 1,2-elimination of HBr. Application of the *Ramberg-Bäcklund* reaction to 9-bromo-8-thiabicyclo[5.2.1]decane-8,8-dioxide (**17**) permits a short synthesis of the *Bredt* olefin bicyclo[5.1.1]non-1(8)-ene (**5**), which can be isolated but shows the typical high reactivity of other methylene-bridged (*E*)-cyclooctenes.

Introduction. – The question of the limits of *Bredt*'s rule is of considerable current interest [1]. It is now generally accepted that the strain and reactivity of a bicyclic or polycyclic bridgehead olefin (*Bredt* olefin) is comparable to those of the corresponding (*E*)-cycloalkene, from which it may be formally derived by bridging. This concept is supported by a large body of experimental evidence [1] [2] and independent force-field calculations [3]. (*E*)-Cyclooctene is a stable, but fairly reactive olefin, and so are the methylene-bridged (*E*)-cyclooctenes bicyclo[3.3.1]-non-1-ene (**1**) [4], bicyclo[4.2.1]non-1-ene (**2**) [5], bicyclo[4.2.1]non-1(8)-ene (**3**) [5], bicyclo[5.1.1]non-1-ene (**4**) [6], and bicyclo[5.1.1]non-1(8)-ene (**5**) [6]. The relative



1 **2** **3** **4** **5**

[1]) Taken in part from the dissertation of *M. Labhart*, Basel 1981.

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[3]) Throughout this paper '1-thiadecalin' will be used in place of 'decahydro-1-thianaphthalene'.

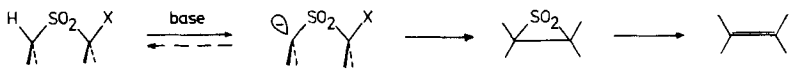
stability and reactivity of methylene-bridged (*E*)-cyclooctenes has been calculated [3], but experimental verification so far has been limited to the readily available olefins **1**, **2** and **3** [7], because the access to the bicyclo[5.1.1]nonenes **4** and **5** *via* pyrolysis of the corresponding bridgehead trimethylammonium hydroxide is lengthy and cumbersome [6]. We therefore sought a more direct synthesis for **5** and report here on a short and fairly efficient preparation of this strained bridgehead olefin by intramolecular *Ramberg-Bäcklund* reaction.

The generally applied synthetic methods for bridgehead olefins [8] did not seem appropriate for the preparation of bicyclo[5.1.1]non-1(8)-ene (**5**). The reductive elimination of a 1,2-dihalide or a related compound would necessitate a lengthy synthesis of a substituted bicyclo[5.1.1]nonane. Rearrangement of a carbenoid precursor is expected to yield a mixture of isomers. The intramolecular *Wittig* reaction [9] is known to fail in the case of cyclobutenes. However, highly strained olefins such as **6** [10] or the cyclobutenes **7** [11], and **8** [12] have been prepared

6 **7** **8**

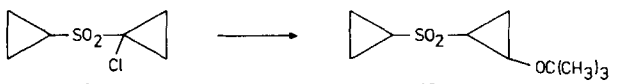
by the intramolecular *Ramberg-Bäcklund* reaction [13], *i.e.* the 1,3-elimination of hydrogen halide followed by sulfur dioxide extrusion starting from an α-halosulfone *(Scheme 1)*. The limit of this method is reached only with rather small and highly strained propellenes and propelladienes of type **8** [14].

Scheme 1



Complications have to be expected in *Ramberg-Bäcklund* reactions when the starting α-halosulfone can undergo competing 1,2-elimination of hydrogen halide. α-Chlorodicyclopropyl sulfone (**9**), *e.g.*, gives none of the anticipated bicyclopropylidene, but the *Michael* adduct **10** of *t*-BuOH to an intermediate cyclopropenyl cyclopropyl sulfone when treated with *t*-BuOK in THF [15]. Chlorosulfone **11** and

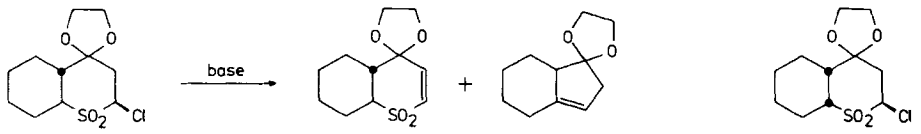
Scheme 2



9 **10**

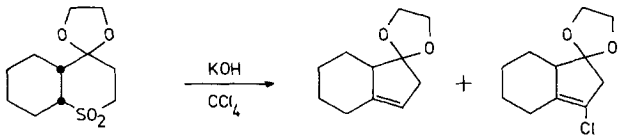
base yield the unsaturated sulfone **12** together with the expected ring contraction product, the hexahydroindene **13** [16]. Clean *Ramberg-Bäcklund* reaction, however, is possible in the case of the isomeric chlorosulfone **14**, which can adopt the favorable W-type arrangement of α-H-, S-, and Cl-atoms *(Scheme 3)* [13]. This is demonstrated by the reaction of sulfone **15** with KOH in CCl_4, which gives a mixture of

Scheme 3



11 12 13 14

Scheme 4



15 13 16

the hexahydroindenes **13** and **16** by the intermediacy of the α-chlorosulfone **14** and the corresponding α,α-dichlorosulfone [17].

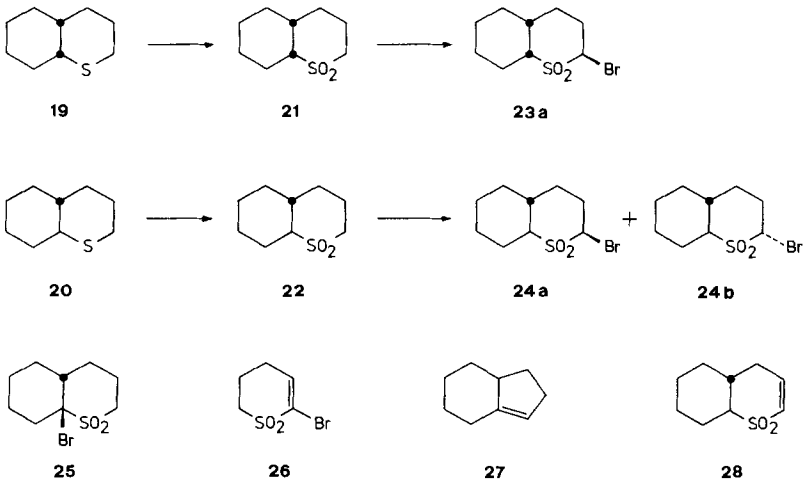
In spite of the discouraging examples above, chances are still intact that base treatment of an α-bromo-(or α-chloro-)sulfone **17** may lead to **5** by *Ramberg-Bäcklund* reaction. It is true that the α-H-, S- and Br-atoms cannot adopt a favorable W-type arrangement in any conformation of the isomers of **17**, but on the other hand, competing 1,2-elimination of HBr is also disfavored because the β-H-atom at the bridgehead and the Br-atom bisect under a dihedral angle of 20–40°, or 80–100°, respectively (estimated from molecular models). In addition, the unsaturated sulfone **18** with a bridgehead double bond is likewise strained, although considerably less than the *Bredt* olefin **5**.

17 18

Intramolecular *Ramberg-Bäcklund* reaction of 2-bromo-1-thiadecalin-1,1-dioxide[3]). – In order to shed more light on the question of competing *Ramberg-Bäcklund* reaction and 1,2-elimination in α-halosulfones and to solve some confusing inconsistencies found by *Kattenberg et al.* with the decalin-type sulfones **11**, **15** and related compounds [16] [17], the preparation and base treatment of 2-bromo-1-thiadecalin-1,1-dioxides was studied. The decalin skeleton simplifies any conformational analysis: In the *trans*-series, a single chair form is present, whereas in the *cis*-series, two interconverting chair conformers have to be considered. Attempted bromination of *cis*- or *trans*-1-thiadecalin (**19** or **20**) with *N*-bromosuccinimide or other brominating (and chlorinating) agents led to an untractable mixture of compounds. Therefore the sulfides **19** and **20** were first oxidized to the corresponding sulfones **21** and **22**, respectively, with etheral *m*-chloroperbenzoic acid. Bromination

was then best performed by the method of *Ziegler & Connor* [18] through deprotonation with ethylmagnesium bromide followed by treatment with elemental bromine. Conversion to the bromosulfones was rather low, but the starting material could be recycled with ease. Deprotonation with BuLi or other strong Li-bases led to isomerization at the ring junction and was therefore rejected. Bromination of *cis*-sulfone **21** gave the *exo*-bromide **23a** as the only isomer in 14% yield. *trans*-Sulfone **22** furnished a mixture of *exo*-bromide **24a** (9%) and *endo*-bromide **24b** (19%). A tertiary bromide (*e.g.* **25**) was not observed. Attempted synthesis of *cis*-9-bromo-1-thiadecalin-1,1-dioxide (**25**) by *Diels-Alder* reaction of butadiene with 2-bromo-1-thia-2-cyclohexene-1,1-dioxide (**26**) failed due to the low dienophilic reactivity of the vinylic bromosulfone.

Scheme 5



The identification of the isomers **a** and **b** rests primarily upon the ^{1}H-NMR. and ^{13}C-NMR. spectra. The proton at C(2) is axial in the case of **24a** and equatorial in **24b**, which gives rise to typical coupling constants with the protons at C(3). Comparison of the ^{13}C-NMR. spectra of all the bromosulfones and the sulfones **21** and **22** allows the conclusion that the isomer formed by bromination of **21** is the *exo*-bromide **23a**, its preferred conformation bearing equatorial Br-atom.

The bromosulfones **23a**, **24a**, and **24b** were subjected to typical *Ramberg-Bäcklund* reaction conditions *(Table)*. Whereas the *cis*-bromosulfone **23a** gives clean 1,3-elimination followed by sulfur dioxide extrusion to the hexahydroindene **27**, only traces of this olefin are obtained from the *trans*-bromosulfones **24a** and **24b**. The main reaction with **24a** and **24b** constitutes the 1,2-elimination to the vinylic sulfone **28** accompanied by bromosulfone isomerization irrespective of the solvent used. This contrasts with the observation of *Kattenberg et al.*, who report preferential *Ramberg-Bäcklund* reaction of the chlorosulfone **11** in dimethyl sulfoxide and 1,2-elimination in dimethoxyethane [16].

Table. *Products formed in the reaction of bromosulfones* **23a**, **24a**, and **24b** *with* t-*BuOK*[a])

Starting material		Solvent	Products			
			Ramberg-Bäcklund reaction  **27**	1,2-Elimination  **28**	Isomerization	Recovered starting material
	**23a**	THF	71%	–	–	20%
		DMSO	52%	–	–	–
	**24a**	THF	0.4%	73%	**23a**: 5%	18%
		DMSO	0.1%	58%	–	36%
	**24b**	THF	0.3%	32%	**24a**: 41%	25%
		DMSO	0.1%	68%	–	10%

[a]) Reaction conditions: Solution 0.02 M in bromosulfone and 0.05 M in *t*-BuOK in the specified solvent, 6 h at – 15° (THF) or + 18° (DMSO), then 18 h at r.t., aq. workup, yields determined by GC.

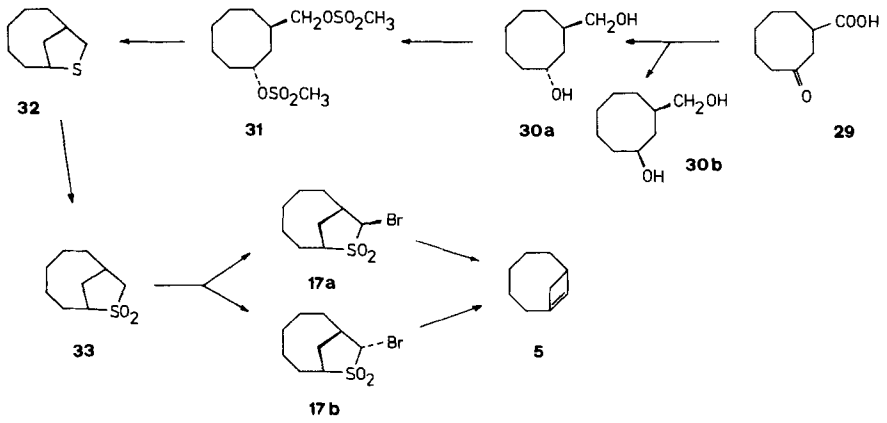
The results presented in the *Table* may be explained as follows: *cis*-bromosulfone **23a** does contain the W-type arrangement of the atoms H–C(9)–SO_2–C(2)–Br which is known to favor 1,3-elimination [13], and therefore gives clean *Ramberg-Bäcklund* reaction. The recovered starting material probably stems from the deprotonation at C(2) instead of C(9). The axial proton at C(9) in **24a** and **24b** seems to be considerably less acidic kinetically, which is in line with observations of diastereomeric deprotonation in other six-membered cyclic sulfones [19][4]). It is also possible that the carbanion formed by deprotonation at C(9) shows high conformational stability, which would slow down 1,3-elimination and isomerization to the *cis*-bromosulfone **23a**. Therefore, deprotonation at C(3) leading to fast 1,2-diaxial elimination of HBr from **24b** and reversible deprotonation at C(2) necessary for isomerization of **24a**/**24b** (*i.e. exo*/*endo*) compete efficiently. The difference in product composition when changing the solvent from THF to DMSO is not very large. Due to better ion solvation in DMSO, the protonation equilibria are somewhat shifted and the reaction rates increased.

Synthesis of bicyclo[5.1.1]non-1(8)-ene *(5).* – Despite the discouraging results with bromosulfones **24a** and **24b**, which led to believe that competing 1,2-elimination may be a serious problem when running a *Ramberg-Bäcklund* reaction in bicyclic halosulfones permitting either reaction type, the synthesis of **5** was attempted.

The known 3-oxocyclooctanecarboxylic acid (**29**) was reduced to a *cis*/*trans*-mixture of diols **30a** and **30b**, which could be separated by crystallization. *trans*-3-(Hydroxymethyl)cyclooctanol (**30a**) was converted to 8-thiabicyclo[5.2.1]decane (**32**) by treatment of the dimethanesulfonate **31** with sodium sulfide in aq. EtOH. Oxidation gave the sulfone **33**, which was brominated with ethylmagnesium bromide and bromine as above. The resulting isomeric bromosulfones **17a** and **17b** were separated by column chromatography and identified by their ^{1}H-NMR. spectra *(Scheme 6).*

[4]) For a general discussion of stereochemical aspects of α-sulfonyl carbanions see [20].

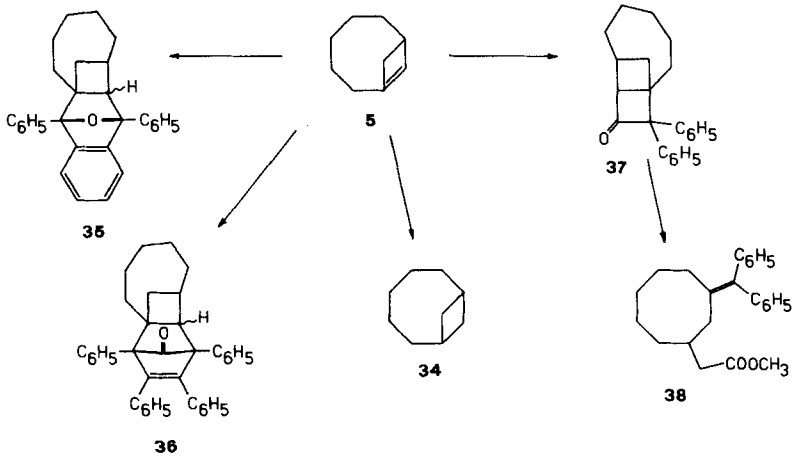
Scheme 6



To our delight, treatment of either *exo*- or *endo*-bromosulfone, **17a** or **17b**, respectively, with *t*-BuOK at −78° gave an acceptable yield (35–49%) of the strained bridgehead olefin **5**, and none of the unsaturated sulfone **18** was detected. The *Ramberg-Bäcklund* reaction works, although an ideal coplanar W-type arrangement of H–C(7)–SO_2–C(9)–Br cannot be reached in **17a** or **17b**. *Bredt* olefin **5** was isolated by aqueous workup of the reaction mixture and chromatography over *Alox* with rigid exclusion of oxygen. The structure of **5** is unambigously proved by spectral methods.

Reactions of bicyclo[5.1.1]non-1(8)-ene. – *Bredt* olefin **5** shows the expected high reactivity towards oxygen, acids and reagents devised for olefin-trapping like the related bridgehead olefins **1**, **2** and **3** [7]. Hydrogenation gives a quantitative yield of bicyclo[5.1.1]nonane (**34**). An *exo*/*endo*-mixture of *Diels-Alder* adducts **35** or **36** is obtained with 1,3-diphenylisobenzofuran and tetraphenylcyclopenta-

Scheme 7



dienone, respectively. The primary product **37** from olefin **5** and diphenylketene proved to be rather labile and underwent ring opening to methyl 3-(diphenylmethylidene)cyclooctaneacetate (**38**) on attempted crystallization from MeOH *(Scheme 7)*.

These preliminary results confirm once more the general observation, that bridged (*E*)-cyclooctenes are isolable but fairly reactive compounds irrespective of the total number of C-atoms or the number of C-atoms in each of the bridges.

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Experimental Part

General remarks. See [21].

cis-*1-Thiadecalin-1,1-dioxide* (**21**). To a solution of cis-*1-thiadecalin* (**19**) [22] (1.51 g, 9.6 mmol) in dry ether under N_2 at 0°, a solution of *m*-chloroperbenzoic acid (4.2 g, 21.7 mmol) in ether was added dropwise. The mixture was stirred overnight at r.t., then washed with cold water, $NaHSO_3$-, $NaHCO_3$-, and NaCl-solution, dried, and evaporated. Recrystallization from hexane gave 1.57 g (87%) of **21**, m.p. 84.5–85°. – IR. (KBr): 2920, 2850, 1445, 1275 and 1110 (SO_2), 1015, 895, 850, 775, 680. – ^{1}H-NMR. ($CDCl_3$): 1.3–2.2 (*m*, 13 H); 2.4 (*m*, H–C(9)); 2.9 (*m*, 2 H–C(2)). – ^{13}C-NMR. ($CDCl_3$): 20.4, 22.4, 22.9, 24.3, 25.2, 31.1 (6*t*); 34.9 (*d*, C(10)); 47.2 (*t*, C(2)); 62.1 (*d*, C(9)).

$C_9H_{16}O_2S$ (188.28) Calc. C 57.43 H 8.57 S 17.03% Found C 57.48 H 8.70 S 16.99%

trans-*1-Thiadecalin-1,1-dioxide* (**22**). Oxidation of trans-*1-thiadecalin* (**20**) [22] with *m*-chloroperbenzoic acid as described above gave **22**, m.p. 115–116° ([23]: m.p. 114–115.8°) in 85% yield. – IR. (KBr): 2930, 2850, 1445, 1285 and 1130 (SO_2), 875, 720. – ^{1}H-NMR. ($CDCl_3$): 1.0–2.3 (*m*, 13 H); 2.49 (*d*×*d*×*d*, *J* = 11.5, 11, 4, H–C(9)); 2.8–3.0 (*m*, 2 H–C(2)). – ^{13}C-NMR. ($CDCl_3$): 20.3 (*t*, C(8)); 23.2 (*t*, C(3)); 24.8 (*t*, C(6)); 25.2 (*t*, C(7)); 32.2 (*t*, C(4)); 32.8 (*t*, C(5)); 39.9 (*d*, C(10)); 51.7 (*t*, C(2)); 65.3 (*d*, C(9)).

$C_9H_{16}O_2S$ (188.28) Calc. C 57.43 H 8.57 S 17.03% Found C 57.41 H 8.69 S 16.99%

2-exo-*Bromo*-cis-*1-thiadecalin-1,1-dioxide* (**23a**). A solution of **21** (0.75 g, 4.0 mmol) in ether (15 ml) and benzene (15 ml) was added dropwise to a solution of ethylmagnesium bromide (5.0 mmol) in ether at 0° under N_2. The mixture was heated to reflux for 3 min. After cooling to 0°, a solution of bromine (0.64 g, 4.0 mmol) in benzene (10 ml) was added. The faintly yellow suspension was stirred for 2 h at r.t., then hydrolyzed with ice-water (20 ml) and worked up as usual. On chromatography over silica gel, benzene/acetone 95:5 eluted first 0.15 g (14%) of a bromosulfone, m.p. 157.5–158°, which was identified as the *exo*-isomer **23a**, then 0.56 g (74%) of the starting material, sulfone **21**. 2-*exo*-Bromo-*cis*-1-thiadecalin-1,1-dioxide (**23a**): IR. (KBr): 2930, 2860, 1445, 1295 and 1120 (SO_2), 930, 820, 770, 650. – ^{1}H-NMR. ($CDCl_3$): 1.3–2.7 (*m*, 13 H); 3.23 (*m*, H–C(9)); 4.73 (*d*×*d*, *J* = 11.5, 4, H–C(2)). – ^{13}C-NMR. ($CDCl_3$): 20.2, 22.4, 25.2, 25.7, 30.6, 34.5 (6 *t*); 34.8 (*d*, C(10)); 57.6 (*d*, C(2)); 62.2 (*d*, C(9)).

$C_9H_{15}BrO_2S$	Calc.	C 40.45	H 5.65	Br 29.91	S 12.00%
(267.19)	Found	„ 40.50	„ 5.71	„ 29.95	„ 11.84%

2-*Bromo*-trans-*1-thiadecalin-1,1-dioxide* (**24**). Compound **22** was deprotonated with ethylmagnesium bromide and brominated as described above. On chromatography over silica gel, benzene/acetone 95:5 eluted 19% of the *endo*-bromide **24b**, 9% of the *exo*-bromide **24a**, and then 72% of the starting material **22**.

2-exo-*Bromo*-trans-*1-thiadecalin-1,1-dioxide* (**24a**): m.p. 144–144.5°. – IR. (KBr): 1310, 1295, 1130, 945, 895, 756, 737, 660. – ^{1}H-NMR. ($CDCl_3$): 1.0–2.0 (*m*, 10 H); 2.4–2.6 (*m*, 3 H); 2.72 (*d*×*d*×*d*, *J* = 11.5, 11, 4, H–C(9)); 4.65 (*d*×*d*, *J* = 11, 4, H–C(2)). – ^{13}C-NMR. ($CDCl_3$): 21.4 (*t*, C(8)); 24.5, 24.7 (2 *t*, C(6) and C(7)); 32.2, 33.3, 34.8 (3 *t*, C(3), C(4) and C(5)); 39.3 (*d*, C(10)); 60.1 (*d*, C(2)); 65.0 (*d*, C(9)).

$C_9H_{15}BrSO_2$ (267.19) Calc. C 40.45 H 5.65 Br 29.91% Found C 40.53 H 5.77 Br 30.02%

2-endo-Bromo-trans-1-thiadecalin-1,1-dioxide (**24b**): m.p. 91–92°. – IR. (KBr): 1310, 1295, 1266, 1125, 795, 765, 720, 665. – ^{1}H-NMR. ($CDCl_3$): 1.1–2.4 (*m*, 12 H); 2.7 (*m*, 1 H); 3.27 (*d*×*d*×*d*, *J* = 12, 11, 4, H–C(9)); 4.92 (*t*, *J* = 3.3, H–C(2)). – ^{13}C-NMR. ($CDCl_3$): 20.1 (*t*, C(8)); 24.8, 25.0 (2 *t*, C(6) and C(7)); 26.6 (*t*, C(4)); 32.3, 32.6 (2 *t*, C(3) and C(5)); 39.7 (*d*, C(10)); 59.2 (*d*, C(2)); 60.9 (*d*, C(9)).

$C_9H_{15}BrO_2S$ (267.19) Calc. C 40.45 H 5.65 Br 29.91% Found C 40.36 H 5.78 Br 30.14%

2-Bromo-1-thia-2-cyclohexene-1,1-dioxide (**26**). A solution of bromine (0.34 g, 2.12 mmol) in CCl_4 (2 ml) was added to a solution of *1-thia-2-cyclohexene-1,1-dioxide* (0.28 g, 2.12 mmol, prepared by a modified procedure of *Fehnel* [24]) in CCl_4 (1 ml). After addition of acetic acid (10 drops), the mixture was stirred for 1 h at r.t. The precipitate was filtered off and recrystallized from ligroin to give 0.34 g (55%) of *trans-2,3-dibromo-1-thiacyclohexane-1,1-dioxide*, white needles, m.p. 180.5–181.5°. – IR. (KBr): 2975, 1435, 1310, 1135, 1050, 1020, 950, 855, 785. – ^{1}H-NMR. (CD_3COCD_3): 2.0–2.7 (*m*, 4 H); 3.45 (*m*, 2 H–C(6)); 4.40 (*t*×*d*, *J* = 11, 4.5, H–C(3)); 5.40 (*d*, *J* = 11, H–C(2)).

$C_5H_8Br_2O_2S$ (291.98) Calc. C 20.56 H 2.76 Br 54.74% Found C 20.48 H 2.69 Br 54.51%

This dibromo compound (0.45 g, 1.5 mmol) in abs. toluene (15 ml) was treated dropwise with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.39 g, 2.5 mmol). After warming to 40° for a few min, the brownish suspension was poured on ice, acidified with 1N H_2SO_4 (6 ml), and worked up with pentane as usual. Recrystallization from ether gave 0.26 g (82%) of **26**, fine needles m.p. 67–68°. – IR. (KBr): 3030, 2920, 1610, 1290, 1130, 885, 710, 620. – ^{1}H-NMR. ($CDCl_3$): 2.2–2.7 (*m*, 4 H); 3.2–3.6 (*m*, 2 H–C(2)); 6.6–6.8 (*m*, H–C(5)).

$C_5H_7BrO_2S$ (211.08) Calc. C 28.44 H 3.34 Br 37.85% Found C 28.39 H 3.39 Br 37.64%

Ramberg-Bäcklund *reaction of bromosulfones* **23a**, **24a** *and* **24b**. Freshly sublimed *t*-BuOK (2.5 equiv.) was dissolved under N_2 in dry THF at −15° or DMSO at +18° (m.p. of this solvent). The bromosulfone dissolved in the same solvent was added dropwise, and the solution (0.02M in bromosulfone and 0.05M in base) stirred for 6 h at −15° or +18°, respectively, then at r.t. overnight. The solution was hydrolyzed with water and extracted with three portions of pentane. The pentane extracts were washed with water and NaCl-solution, dried over $MgSO_4$, and analyzed by GC. (*SE 52*, 100–200°) after addition of undecane as an internal standard. *2,4,5,6,7,7a-Hexahydroindene* (**27**) was identified by comparison with an authentic sample [25].

trans-*1,4,5,6,7,8,9,10-Octahydro-1-thianaphthalene-1,1-dioxide* (**28**). Compound **24b** (0.30 g, 1.1 mmol) was treated with *t*-BuOK in DMSO as described above. Chromatography on silica gel with ether/petroleum ether (3:2) gave 90 mg (44%) of vinylsulfone **28**, m.p. 106–107°, needles from hexane. – IR. (CCl_4): 3030, 2930, 2860, 1650, 1450, 1315 and 1130 (SO_2), 895, 710, 665. – ^{1}H-NMR. ($CDCl_3$): 0.8–2.3 (*m*, 11 H); 2.90 (*t*×*d*, *J* = 12, 4, H–C(9)); 6.40 (*m*, H–C(2) and H–C(3)).

$C_9H_{14}O_2S$ (186.28) Calc. C 58.03 H 7.58 S 17.21% Found C 57.82 H 7.56 S 17.03%

3-(Hydroxymethyl)cyclooctanol (**30**). *3-Oxocyclooctanecarboxylic acid* (**29**) (2.42 g, 14.2 mmol, prepared according to *Hirsch & Cross* [26]) dissolved in dry ether (30 ml) and THF (5 ml) was added dropwise under N_2 to a suspension of $LiAlH_4$ (0.86 g, 22.7 mmol) in abs. ether (50 ml) at 0°. The mixture was boiled with reflux for 1 h, then cooled and hydrolyzed by dropwise addition of 1N NaOH (3.4 ml). The white precipitate was filtered off. The filtrate was evaporated and distilled at 112–126°/0.025 Torr to give 1.50 g (67%) of **30**, viscous oil, 3:2 mixture of *cis*- and *trans*-isomers **30b** and **30a**. – IR. (film): 3330, 2920, 2855, 1467, 1445, 1078, 1048, 1027, 1008. – ^{1}H-NMR. ($CDCl_3$): 1.2–2.3 (*m*, 13 H); 2.83 (br. *s*, 2 OH); 3.4 (*d*, *J* = 4, CH_2OH); 3.9 (*m*, H–C(1)).

$C_9H_{18}O_2$ (158.24) Calc. C 68.11 H 11.67% Found C 68.31 H 11.47%

On repeated crystallization from CH_2Cl_2, the *cis*-isomer **30b**, m.p. 89–90.5°, could be obtained pure. Its identification rests on the fact that this isomer was obtained in pure state by reduction of the lactone of 3-hydroxycyclooctanecarboxylic acid [27].

trans-*3-(Methanesulfonyloxy)cyclooctanemethyl methanesulfonate* (**31**). To a solution of *trans*-diol **30a** (9.8 g, 62.7 mmol, impure material containing 15% of the *cis*-diol **30b**) and methanesulfonyl chloride (15.8 g, 138 mmol) in CH_2Cl_2 (400 ml) at −15°, triethylamine (12.69 g, 125.4 mmol) was added dropwise during 2 h. After stirring for additional 30 min at −15°, the reaction mixture was worked up as usual. The dimethanesulfonate **31** (19.7 g, 100%) was used for the next step without

purification. – IR. (film): 2930, 2855, 1462, 1348 and 1171 (OSO_2), 901. – ^{1}H-NMR. (CCl_4): 1.3–2.2 (*m*, 13 H); 2.94 (*s*, 6 H); 3.95 (*d*, *J* = 5, 2 H–C(1')); 4.9 (*m*, H–C(3)).

8-Thiabicyclo[5.2.1]decane (**32**). To a solution of sodium sulfide pentahydrate (10.5 g, 62.4 mmol) in 80% aq. EtOH (150 ml), a solution of above crude dimethanesulfonate **31** (19.7 g, 62.7 mmol) in EtOH (45 ml) and THF (45 ml) and at the same time an additional equivalent of sodium sulfide (10.5 g, 62.4 mmol) in 80% aq. EtOH (90 ml) were added dropwise from a syringe driver during 12 h. The mixture was boiled for additional 4 h, then distilled with steam. The distillate was extracted with petroleum ether, the extracts dried and distilled. The fraction b.p. 52–75°/0.02 Torr was chromatographed (silica gel, 1% CH_2Cl_2 in petroleum ether) and sublimed at 40°/0.015 Torr to give 1.73 g (18%) of **32** as a waxy, hygroscopic solid. – IR. (film): 2920, 2855, 1467, 1445, 1195. – ^{1}H-NMR. ($CDCl_3$): 1.6–2.2 (*m*, 12 H); 2.6 (*m*, H–C(1)); 2.68 (*d*×*d*, *J* = 10, 1.2, H_{endo}–C(9)); 3.00 (*d*×*d*, *J* = 10, 6.5, H_{exo}–C(9)); 3.70 (*m*, H–C(7)). – ^{13}C-NMR. ($CDCl_3$): 23.8, 24.1 (2 *t*, C(3) and C(4)); 28.9, 32.3 (2 *t*, C(2) and C(5)); 38.3 (*t*, C(9)); 38.7, 38.7 (2 *t*, C(6) and C(10)); 41.1 (*d*, C(1)); 45.9 (*d*, C(7)).

$C_9H_{16}S$ (156.28) Calc. C 69.19 H 10.32% Found C 68.61 H 10.48%

Other fractions contained 8-oxabicyclo[5.2.1]decane, a cyclooctenemethyl ethyl ether, and a cyclooctenemethyl ethyl sulfide in amounts of 5–12%.

8-Thiabicyclo[5.2.1]decane-8,8-dioxide (**33**). Compound **32** was oxidized with *m*-chloroperbenzoic acid as described for **21**. Sublimation at 120°/0.04 Torr gave 86% of **33** as a waxy solid. – IR. (CCl_4): 2920, 2850, 1460, 1305 and 1110 (SO_2). – ^{1}H-NMR. ($CDCl_3$): 1.6–2.2 (*m*, 10 H); 2.3–2.9 (*m*, H–C(1) and 2 H–C(10)); 2.95–3.35 (*m*, H–C(7) and 2 H–C(9)). – ^{13}C-NMR. ($CDCl_3$): 23.8, 24.3, 27.7, 28.4, 29.7 (5 *t*); 31.9 (*d*, C(1)); 33.1 (*t*, C(10)); 56.1 (*t*, C(9)); 58.5 (*d*, C(7)).

$C_9H_{16}O_2S$ (188.28) Calc. C 57.43 H 8.57 S 17.03% Found C 57.31 H 8.81 S 17.21%

9-Bromo-8-thiabicyclo[5.2.1]decane-8,8-dioxide (**17**). Dioxide **33** was deprotonated with ethylmagnesium bromide and brominated as described for **23a**. On chromatography on silica gel with CH_2Cl_2, 0.64 g (57%) of a 2:1 mixture of *exo*- and *endo*-bromosulfone, **17a** and **17b**, respectively, and 0.19 g (24%) of starting material **33** were obtained. Crystallization from cyclohexane gave pure *endo*-isomer **17b**. The *exo*-isomer **17a** could be isolated pure by chromatography of the mother liquors with benzene/acetone 98:2.

9-exo-Bromo-8-thiabicyclo[5.2.1]decane-8,8-dioxide (**17a**): m.p. 73–74° (from hexane/ether). – IR. (KBr): 2900, 2860, 1460, 1310 and 1135 (SO_2); 745, 620. – ^{1}H-NMR. ($CDCl_3$): 1.4–2.8 (*m*, 13 H); 3.36 (*m*, H–C(7)); 4.7 (*d*×*d*, *J* = 3.7, 1, H–C(9)). – ^{13}C-NMR. ($CDCl_3$): 24.0, 25.6, 27.3, 28.0, 28.0, (5 *t*); 31.1 (*t*, C(10)); 43.6 (*d*, C(1)); 58.0 (*d*, C(7)); 62.6 (*d*, C(9)).

$C_9H_{15}BrO_2S$ (267.19) Calc. C 40.45 H 5.66 Br 29.91% Found C 40.41 H 5.86 Br 29.81%

9-endo-Bromo-8-thiabicyclo[5.2.1]decane-8,8-dioxide (**17b**): m.p. 113–114° (from cyclohexane). – IR. (KBr): 2940, 2860, 1465, 1305 and 1110 (SO_2), 685. – ^{1}H-NMR. ($CDCl_3$): 1.1–2.9 (*m*, 13 H); 3.2–3.5 (*m*, H–C(7)); 5.35 (*d*, *J* = 6, H–C(9)). – ^{13}C-NMR. ($CDCl_3$): 23.2, 23.7, 26.5, 27.1, 27.7 (5 *t*); 30.3 (*t*, C(10)); 38.7 (*d*, C(1)); 56.4 (*d*, C(7)); 68.2 (*d*, C(9)).

$C_9H_{15}BrO_2S$ (267.19) Calc. C 40.45 H 5.66 S 11.99% Found C 40.53 H 5.79 S 11.88%

Bicyclo[5.1.1]non-1(8)-ene (**5**). A solution of freshly sublimed *t*-BuOK (3.9 g, 34.7 mmol) in dry THF (150 ml) was added dropwise during 6 h to **17** (2.05 g, 7.67 mmol, mixture of *exo*- and *endo*-isomers) in dry THF (150 ml) at −75° under N_2. The reaction mixture was stirred at −75° for additional 5 h, then warmed to r.t., hydrolyzed with oxygen-free water (30 ml), and extracted with pentane. The pentane extracts were washed with water and NaCl-solution (always with rigid exclusion of oxygen in a dry box), dried over $MgSO_4$, and carefully concentrated. The crude material was chromatographed over neutral *Alox* with pentane to remove traces of THF and *t*-BuOH, then distilled at 100°/13 Torr in a bulb tube to give 0.20 g (21%) of **5** as an oil, solidifying at *ca.* 10°. In other experiments, yields up to 35% (from *exo*-bromide **17a**) and 49% (from *endo*-bromide **17b**) were found (determined by GC. of the crude material). – IR. (film): 3030, 2920, 2850, 1615, 1460, 1440, 1280, 940, 800. – UV. (cyclohexane): λ_{max} 203 nm (logε 3.5). – ^{1}H-NMR. (C_6D_6): 0.9–3.0 (*m*, 13 H); 5.84 (*m*, H–C(8)). – ^{13}C-NMR. (C_6D_6): 27.2, 27.9, 32.5, 33.0, 33.9, 37.0 (6 *t*); 38.9 (*d*, C(7)); 137.5

(*d*, C(8)); 154.8 (*s*, C(1)). – MS.: 122 (19, M^+), 107 (14), 93 (28), 79 (41), 67 (18), 59 (41), 43 (100), 42 (85), 41 (77).

C_9H_{14} (122.21) Calc. C 88.45 H 11.55% Found C 88.05 H 11.58%

Bicyclo[5.1.1]nonane (**34**). Olefin **5** (60 mg) in benzene (2 ml) was hydrogenated over 10% Pd/C (5 mg). The catalyst was filtered off, and the filtrate distilled in a bulb tube (100°/50 Torr) to give 60 mg (98%) of **34** as a waxy, extremely volatile solid. – IR. (film): 2910, 2840, 1460, 1440. – ^{1}H-NMR. (C_6D_6): 1.5–2.1 (*m*, 12 H); 2.2–2.6 (*m*, 4 H). – ^{13}C-NMR. (C_6D_6): 26.3 (*t*, C(4)); 28.7, 29.2 (2 *t*, C(2), C(3), C(5), and C(6)); 29.9 (*d*, C(1) and C(7)); 34.5 (*t*, C(8) and C(9)). – MS.: 124 (2, M^+), 96 (56), 81 (76), 67 (100), 54 (90), 41 (86), 28 (41).

C_9H_{16} (124.22) Calc. C 87.02 H 12.98% Found C 86.68 H 12.89%

2,5-Diphenyl-3,4-benzo-14-oxatetracyclo[5.5.1.1^{2,5}.0^{1,6}]tetradec-3-ene (**35**). Dioxide **17** (0.270 g, 1.01 mmol) and 1,3-diphenylisobenzofuran (0.270 g, 1.00 mmol) were treated with *t*-BuOK (0.376 g, 3.35 mmol) in THF at −75° as described above. Maleic anhydride (0.10 g, 1.0 mmol) was added to trap the excess 1,3-diphenylisobenzofuran. The reaction mixture was stirred for 2 h at r.t., evaporated in vacuo, then dissolved in 75% aq. EtOH 1N in NaOH, and boiled for 4 h to hydrolyze the carboxylic anhydrides. The usual workup followed by chromatography on silica gel with benzene gave 0.210 g (53%) of the *Diels-Alder* adduct **35** as a 9:1-mixture of *exo*- and *endo*-isomers (determined by NMR.).

exo-**35**: m.p. 125–127° (from EtOH). – IR. (KBr): 3095, 3070, 3040, 2920, 2860, 1600, 1475, 1445, 1300, 980, 745, 700, 675. – ^{1}H-NMR. ($CDCl_3$): 0.7–2.3 (*m*, 13 H); 2.49 (*s*, H–C(6)); 6.8–7.7 (*m*, 14 H). – ^{13}C-NMR. ($CDCl_3$): 25.3 (*d*, C(7)); 25.9, 28.1, 29.0, 30.4, 33.5, 34.2 (6 *t*); 50.9 (*s*, C(1)); 52.7 (*d*, C(6)); 89.7, 92.5 (2 *s*, C(2) and C(5)); 118.4, 121.0, 126.0, 126.6, 127.1 (2 C); 128.0 (6 C); 128.3 (2 C) (14 *d*); 136.3, 137.3 (2 *s*); 145.3, 148.8 (2 *s*, C(3) and C(4)).

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19 Found C 88.71 H 7.39%

endo-**35**. – ^{1}H-NMR. ($CDCl_3$): 3.05 (*s*, H–C(6)). – ^{13}C-NMR. ($CDCl_3$): 51.2 (*s*, C(1)); 52.1 (*d*, C(6)); 86.6, 95.0 (2 *s*, C(2) and C(5)); 147.1, 148.2 (2 *s*, C(3) and C(4)).

2,3,4,5-Tetraphenyltetracyclo[5.5.1.1^{2,5}.0^{1,6}]tetradec-3-en-14-one (**36**). An acetone solution of **5** was treated with a solution of tetraphenylcyclopentadienone, until a faint reddish color persisted. Chromatography on silica gel with benzene gave the *Diels-Alder* adduct **36** as a 3:1-mixture of *exo*- and *endo*-isomers (determined by NMR.).

exo-**36**: m.p. 150–155° (from EtOH). – IR. (KBr): 3060, 3030, 2920, 2850, 1770, 1600, 1495, 1445, 700. – ^{1}H-NMR. (C_6D_6): 1.0–2.3 (*m*, 11 H); 2.4–3.0 (*m*, 2 H); 3.37 (br. *s*, H–C(6)); 6.6–7.8 (*m*, 20 H). – ^{13}C-NMR. (C_6D_6): 25.6, 29.7, 30.5 (2 C); 33.5 (5 *t*); 34.3 (*d*, C(7)); 36.1 (*t*, C(13)); 44.8 (*d*, C(6)); 46.7 (*s*, C(1)); 67.7, 68.0 (2 *s*, C(2) and C(5)); 126.8–137.4 (24 C); 144.0, 145.0 (2 *s*, C(3) and C(4)); 198.4 (*s*, C(14)).

$C_{38}H_{34}O$ (506.71) Calc. C 90.07 H 6.76% Found C 90.27 H 6.69%

endo-**36**. – ^{1}H-NMR. (C_6D_6): 2.69 (br. *s*, H–C(6)). – ^{13}C-NMR. (C_6D_6): 47.0 (*s*, C(1)); 51.2 (*d*, C(6)); 142.1, 145.2 (2 *s*, C(3) and C(4)); 202.8 (*s*, C(14)).

10,10-Diphenyltricyclo[5.3.1.0^{1,8}]undecan-9-one (**37**). Olefin **5** (110 mg, 0.90 mmol) in abs. benzene (10 ml) was treated with a solution of diphenylketene (200 mg, 1.0 mmol) in benzene under Ar. After 2 h at r.t., the mixture was evaporated and chromatographed on silica gel with benzene/cyclohexane to give 270 mg (95%) of the diphenylketene adduct **37**. – IR. (film): 3060, 3030, 2930, 2860, 1730 (C=O), 1660, 1600, 1470, 1445, 705. – ^{1}H-NMR. (CCl_4): 1.2–2.6 (*m*, 12 H); 3.44 (*d*, *J* = 2, H–C(8)); 7.0–7.8 (*m*, 10 H).

Methyl 3-(diphenylmethylidene)cyclooctaneacetate (**38**). The crude diphenylketene adduct **37** (270 mg, 0.85 mmol) was dissolved in hot MeOH. Distillation at 240°/0.08 Torr in a bulb tube gave 150 mg (48%) of **38** as a colorless oil. – IR. (film): 3080, 3060, 3030, 2930, 2860, 1735 ($COOCH_3$), 1600, 1490, 1445, 1150, 705. – ^{1}H-NMR. ($CDCl_3$): 1.1–2.6 (*m*, 15 H); 3.46 (*s*, 3 H); 7.0–7.4 (*m*, 10 H). – ^{13}C-NMR. ($CDCl_3$): 24.9, 25.9, 26.9, 32.7, 32.8 (5 *t*); 34.2 (*d*, C(1)); 38.2, 42.2 (2 *t*, C(2) and C(1′)); 51.1 (*qa*, OCH_3); 126.0, 128.2, 128.8 (10 *d*); 138.2, 138.5 (2 *s*); 143.6, 143.7 (2 *s*, C(3) and C(1″)); 173.0 (*s*, CO).

$C_{24}H_{28}O_2$ (348.49) Calc. C 82.72 H 8.10% Found C 82.63 H 8.14%

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