Sulfonyl-Stabilized Allylic Norbornenyl and Norbornyl Carbanions: Structure and Stereoselectivity of Reaction with Electrophiles

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The structures of the norbornenyl and norbornyl sulfones *exo*-**5**, *endo*-**5** and *endo*-**6** have been determined experimentally, by X-ray analysis, and theoretically by ab initio calculations (HF/6–31+G*). X-ray crystal structure analyses of the lithiated allylic norbornenyl and norbornyl sulfones *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme revealed dimeric O–Li contact ion pairs devoid of C–Li bonds. The anions of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme adopt both the *endo* conformation (C2–S) and are characterized by in the *exo* direction pyramidalized anionic C atoms. The degree of pyramidalization of the C2 atom of **3** is higher than that of **4**. Ab initio optimizations (HF/6–31+G*) of the structures of the anions of methylenenorbornene **I** and methylenenorbornane **II** resulted in local minima featuring non-planar C2 atoms which are pyramidalized in the *exo* direction in both cases, but to different degrees. In both cases cryoscopy of **3** and **4** in THF at –108.5 °C revealed approximately 1:1 mixtures of monomers and dimers. The sulfones *exo*-**5**, *endo*-**5**, *exo*-**6** and *endo*-**6** as well as the lithiosulfones **3** and **4** were studied by NMR spectroscopy. ^{1}H-NMR (400 MHz), ^{13}C-NMR (100 MHz) and ^{6}Li-NMR (44 MHz) spectroscopy of **3** and **4** at –100 °C in [D]$_8$THF revealed in each case only one set of signals, independent of the configuration of the starting sulfones. This indicates in both cases that attainment of both the monomer-dimer and the *endo*/*exo* equilibria of **3** and **4** is fast on the NMR time scale. According to ^{6}Li{^{1}H}- and ^{1}H{^{1}H}-NOE experiments of **3** and **4** the monomeric and dimeric species *endo*-**3** and *endo*-**4**, having *endo* anions, seem to be preferred in THF solution. Ab initio calculations of the anions of **3** and **4** resulted in structures *endo*-**3**(–Li$^+$), *exo*-**3**(–Li$^+$), *endo*-**4**(–Li$^+$) and *exo*-**4**(–Li$^+$) (HF/6–31+G*), whose atomic point charges were calculated by the method of Kollman et al. The C2 atoms of *endo*-**3**(–Li$^+$) and *endo*-**4**(–Li$^+$) are pyramidalized in the *exo* direction whereas the C2 atoms of *exo*-**3**(–Li$^+$) and *exo*-**4**(–Li$^+$) are pyramidalized in the *endo* direction. According to the calculations, the *endo* anions are more stable than the *exo* anions. There is good agreement between the optimized structures of the free anions and the experimentally determined structures of the anions of the contact ion pairs in the crystal. Reactions of **3** and **4** with DX, MeI, EtI, *n*PrI and *n*HeI occurred at the C2 atom under the selective formation of the corresponding *endo*sulfones *endo*-**8a–e** and *endo*-**9a–e**, respectively, in all cases. Thus, an earlier report on the selective formation of the *exo*sulfone *exo*-**9b** in the reaction of **4** with MeI has to be revised. Product ratios were independent of the configuration of the starting sulfones and varied with the nature of the electrophile. Selectivities were highest in the case of the norbornyl species **4**. Reaction of **3** with PhCHO occurred at the α position (C2) to afford the alcohols *endo*-**8f** and *exo*-**8f** (88:12) as single diastereomers and at higher temperatures at the γ position (C8), whereas reaction of **4** with PhCHO took place at the γ position even at low temperatures. Methylation of *endo*-**5** and *exo*-**5** at –105 °C by both the stepwise method and by the in situ method gave different ratios of *exo*- and *endo*-methylation products. The selectivities of reaction of **3** and **4** with electrophiles have been rationalized by the Curtin-Hammett/Winstein-Holness concepts. It is proposed that *endo*-**3** (*endo*-**4**) and *exo*-**3** (*exo*-**4**) are conformationally labile on the time scale defined by the rate of their reactions with electrophiles, and are attacked by electrophiles with high selectivities from the *exo* and the *endo* face, respectively, because of the shielding by the phenyl group and the direction of the pyramidalization of the anionic C atom. Preferential formation of the *endo* sulfones is thus ascribed to *exo* attack of electrophiles on *endo*-**3** (*endo*-**4**) being faster than *endo* attack on *exo*-**3** (*exo*-**4**) because of Houk's staggering effect. Methylation of **3** and **4** by the in situ method showed **3**, whose C2 atom is stronger pyramidalized, to be more reactive than **4**. The base-catalyzed H/D exchange of sulfones *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6** with NaOCD$_3$ in CD$_3$OD proceeded in all cases with a high degree of retention of configuration.

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Introduction

Norbornenyl and norbornyl carbanions of type **1** (Scheme 1), carrying a stabilizing functional group in the 2 position, have attracted much interest for both synthetic and stereochemical reasons.[1–8] Reactions of **1** with electrophiles generally proceed in a highly *exo*-selective fashion (product has the functional group in the *endo* position) irrespective of the configuration of the corresponding carbon acid and the nature of the functional group. The origin of the *exo* selectivity and its configurational invariance are, however, only

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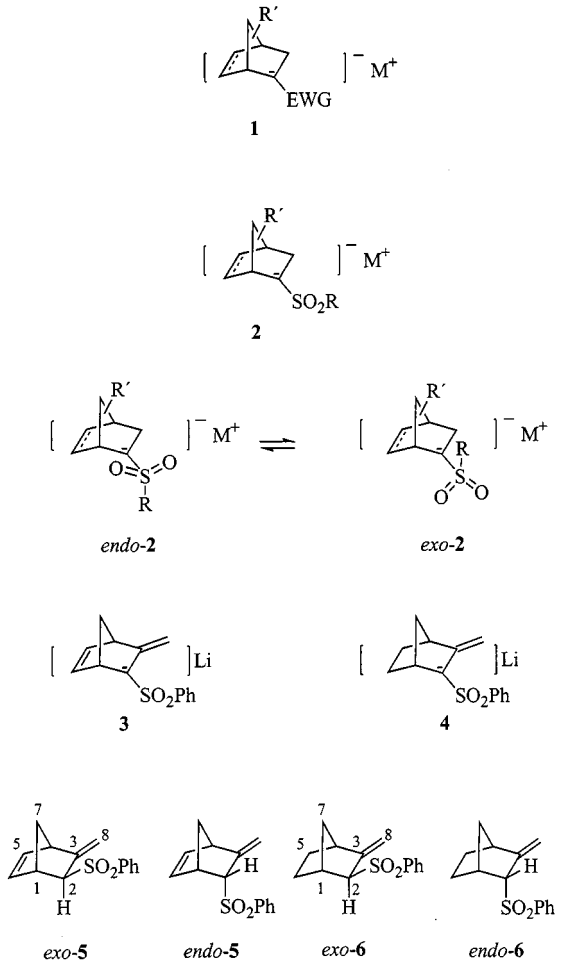


Scheme 1. Sulfonyl-stabilized 2-norbornenyl and 2-norbornyl anions

poorly understood. This seems to be at least in part due to the scarcity of information concerning the structure of **1**,[9] which is in sharp contrast to the wealth of knowledge on the structure of norbornenyl and norbornyl cations.[10] A particularly stereochemically interesting subclass of **1** encompasses the α-sulfonyl carbanions **2**[6] which, in principal, can adopt the two conformations: *endo*-**2** and *exo*-**2**.[11,12a−b] The possible existence of diastereomers *endo*-**2** and *exo*-**2** raises several pertinent stereochemical questions. (1) Which height do the barriers for the *endo*/*exo* equilibration have, and what is the position of the *endo*/*exo* equilibrium? (2) How do the sulfonyl group and the bicyclic ring skeleton exert control over the reactivity of the diastereomers towards electrophiles and the interplay between that and the stereochemical control ? (3) Are the anionic C atoms of the diastereomers planar? (4) If not, in which direction are the anionic C atoms pyramidalized? In order to obtain more specific information on these questions the allylic carbanions **3** and **4** have been studied, which were selected for several reasons. Trost et al. had reported on a stereochemical dichotomy in the methylation of **3** and **4**.[6e] While reaction of the norbornenyl species **3** with methyl iodide gave the corresponding *endo* sulfone preferentially, that of the norbornyl species **4** with methyl iodide preferentially yielded the corresponding *exo* sulfone. This was rationalized by proposing that **3** and **4** adopt opposing conformations of type *endo*-**2** and *exo*-**2**, respectively, featuring C−Li and O−Li bonds. It remained unclear, however, as to why **3** and **4** should exhibit such a structural divergence. Second, lithioallyl sulfones have gained considerable importance in organic synthesis.[13][14] However, only little is known about their structure.[15−18] It is particularly desirable to have knowledge of the mode of coordination between the Li atom and the allylic α-sulfonyl carbanion in the contact ion pair in order to gain a better understanding of the high regioselectivity of their reaction with electrophiles. X-ray crystal structure analysis of an acyclic lithioallyl sulfone had revealed a coordination of the Li atom only by the O atom but not by the C atoms of the allylic moiety.[16] However, because of the *syn* position of the sulfonyl group and the exocyclic double bond in **3** and **4**, a coordination of the Li atom not only by the O atom but also by the allylic moieties might be enforced, and thus be amenable to scrutiny. Thus, it was hoped that an investigation of **3** and **4** would not only help to answer the aforementioned stereochemical questions concerning **2,** but also yield information as to the structure of lithioallyl sulfones in general.

In this paper efforts to elucidate the structure and reactivity of **3** and **4** by using sulfones *exo*-**5**, *endo*-**5**, *endo*-**6** and *exo*-**6**[19] as the starting carbon acid[20] are described.

Results and Discussion

1. Structure of the Sulfones

We began the structural investigation of **3** and **4** by the determination of the crystal structures of sulfones *exo*-**5**, *endo*-**5** and *endo*-**6** by X-ray analysis (see Figures 1−3).[21][22] The bonding parameters of *exo*-**5**, *endo*-**5** and *endo*-**6** are in the normal range and show no peculiarities[23] (Table 1). Presumably due to steric reasons, the phenylsulfonyl group adopts a C2−S conformation in which the phenyl group is *anti* to the exocyclic double bond in all three sulfones, as revealed by the values of the torsion angle C9−S−C2−C3.[23] Intuitively one assumes that due to less steric crowding the *exo* isomers of **5** and **6** are somewhat more stable than the corresponding *endo* isomers. To estimate the relative stability of the *exo* and *endo* isomers of **5**

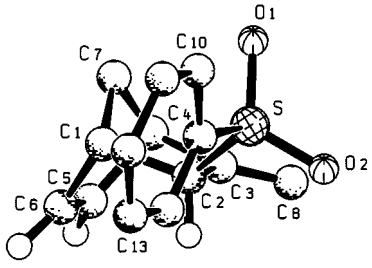


Figure 1. Crystal structure of *exo*-**5**

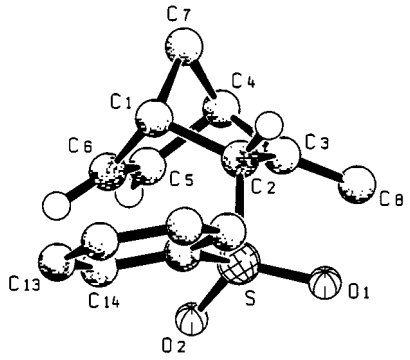


Figure 2. Crystal structure of *endo*-**5**

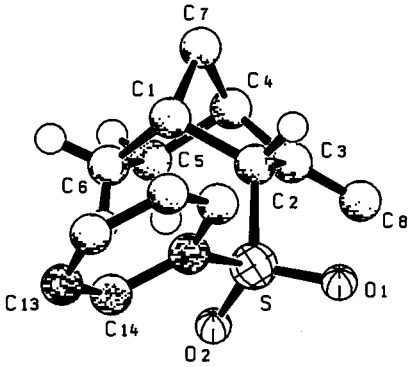


Figure 3. Crystal structure of *endo*-**6**

and **6**, and because of structural reasons (vide infra), complete geometry optimizations for the four sulfones at the one-determinant (Hartree-Fock, HF) level of ab initio theory with the 6−31G* basis set were performed. Some optimized structural parameters of interest are listed in Table 1 together with the corresponding experimental results for the molecules in the crystal. At this level of theory the *endo* isomers of **5** and **6** are 1.7 kcal/mol and 1.9 kcal/mol higher in energy than the corresponding *exo* isomers. When correlation energy calculated by means of Møller-Plesset perturbation theory to the second order (MP2) is added in single point calculations (MP2/6−31+G*//HF/6−31+G*) the energy difference is slightly reduced to 1.5 kcal/mol for **5** and 1.7 kcal/mol for **6**. The calculated values for the energy difference between sulfones *endo*-**5** and *exo*-**5** as well as sulfones *endo*-**6** and *exo*-**6** in the gas-phase compare favorably with the results of a base-catalyzed equilibration of the sulfones, which in the case of the norbornenyl sulfones gave a mixture of *exo*-**5** and *endo*-**5** in a ratio of 76:24, and in that of the norbornyl sulfones a mixture of *exo*-**6** and *endo*-**6** in a ratio of 86:14 (vide infra).

On the basis of the unequivocal determination of the configurations of *exo*-**5**, *endo*-**5** and *endo*-**6** by X-ray structure analysis, a complete assignment of the signals in the NMR spectra of *exo*-**5**, *endo*-**5**, *endo*-**6** and *exo*-**6** was accomplished by NOE experiments and two-dimensional methods (H,H-COSY, C,H-COSY) (Tables 2−4). The signs of the $\Delta\delta$ (^{1}H) values on going from the *endo* to the *exo* isomers are the same for the norbornenyl system **5** and the norbornyl system **6**. Because of the anisotropy effect of the SO_2 group, the signal for 7-H_{syn} of *exo*-**6** is significantly shifted downfield as compared to that of *endo*-**6** whereas it is the signal of 6-H_{endo} of *endo*-**6** which is shifted downfield as compared to that of *exo*-**6**.[6f,6h,24] Similar differences exist in the ^{1}H-NMR spectra of *exo*-**5** and *endo*-**5** in regard to the signals of 7-H_{syn}. Thus, in solution the phenylsulfonyl group in *exo*-**5**, *endo*-**5**, *exo*-**6** and *endo*-**6** most likely preferentially adopts a similar C2−S conformation as in the crystal.

Table 1. Selected bond lengths [Å], bond angles [°] and absolute values of dihedral angles [°] of sulfones *exo*-**5**, *endo*-**5** and *endo*-**6** as well as of lithiosulfones *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme; the numbers in square brackets are structural parameters calculated at the HF/6−31G* level

	exo-**5**	*endo*-**5**	*endo*-**3**/ ent-*endo*-**3**·2diglyme	*endo*-**6**	*exo*-**6**[a]	*endo*-**4**/ ent-*endo*-**4**·2diglyme
S−C2	1.794(4) [1.802]	1.790(6) [1.798]	1.649(7)	1.776(2) [1.799]	[1.803]	1.633(3)
S−C9	1.769(4) [1.776]	1.782(6) [1.776]	1.783(4)	1.761(3) [1.775]	[1.776]	1.778(3)
S−O1	1.444(3) [1.439]	1.451(5) [1.440]	1.444(3)	1.436(2) [1.440]	[1.439]	1.443(2)
S−O2	1.438(3) [1.440]	1.436(4) [1.436]	1.453(3)	1.442(2) [1.438]	[1.440]	1.452(2)
C2−C3	1.532(6) [1.535]	1.521(9) [1.534]	1.440(9)	1.530(4) [1.534]	[1.534]	1.434(4)
C3−C8	1.302(7) [1.316]	1.33(1) [1.316]	1.320(8)	1.319(4) [1.317]	[1.317]	1.333(6)
C5−C6	1.324(7) [1.322]	1.31(1) [1.321]	1.28(1)	1.550(5) [1.555]	[1.557]	1.483(6)
O1−Li1	−	−	1.913(7)	−	−	1.916(5)
O2−Li1	−	−	1.935(7)	−	−	1.930(5)
C1−C2−C3	101.7(3) [101.6]	102.2(5) [102.0]	107.5(5)	102.5(2) [102.4]	[101.9]	107.0(3)
C1−C2−S	115.0(3) [115.3]	116.9(4) [117.3]	119.1(5)	118.6(2) [119.1]	[115.1]	122.7(2)
C3−C2−S	112.0(3) [112.9]	112.7(4) [115.1]	123.2(3)	113.9(2) [114.0]	[112.7]	125.5(3)
C2−C3−C4	104.7(4) [104.8]	105.3(5) [104.5]	102.1(5)	104.5(2) [104.9]	[105.3]	102.2(3)
C2−C3−C8	128.0(4) [127.7]	127.7(6) [128.0]	132.4(7)	127.4(3) [127.6]	[127.2]	132.9(4)
O−S−O	118.2(2) [120.1]	119.3(3) [120.1]	116.7(2)	118.3(1) [119.7]	[120.1]	116.8(1)
C9−S−C2−C1	59.0(3) [64.8]	59.0(5) [62.7]	67.2(4)	46.9(2) [56.3]	[64.9]	73.0(3)
C9−S−C2−C3	174.4(3) [179.0]	177.0(4) [177.3]	73.8(4)	167.6(2) [177.4]	[178.8]	79.5(3)
S−C2−C3−C8	55.1(6) [54.1]	51.3(8) [49.4]	31.6(9)	43.5(3) [48.1]	[55.6]	17.9(6)

[a] No experimental data available: See text.

Table 2. ^{1}H-NMR data (δ_H, ppm) of sulfones *exo*-**5**, *endo*-**5**, *exo*-**6** and *endo*-**6** in $CDCl_3$ as well as of lithiosulfones **3** and **4** in $[D]_8$THF at 25°C

	exo-**5**	*endo*-**5**	**3**	$\Delta\delta_1/\Delta\delta_2$[a]	*exo*-**6**	*endo*-**6**	**4**	$\Delta\delta_1/\Delta\delta_2$[a]
H-1	3.16	3.03	3.40	+0.24/+0.37	2.64	2.37	2.92	+0.18/+0.55
H-2	3.50	4.20	–	–	3.59	4.03	–	–
H-4	3.28	3.29	2.97	−0.31/−0.32	2.79	2.84	2.51	−0.28/−0.33
H_{exo}-5	6.28	6.13	5.66	−0.62/−0.47	1.65	1.75	1.42	−0.23/−0.33
H_{endo}-5	–	–	–	–	1.32	1.57	1.00	−0.32/−0.57
H_{exo}-6	6.09	6.06	5.80	−0.29/−0.26	1.65	1.40	1.42	−0.13/+0.02
H_{endo}-6	–	–	–	–	1.22	2.37	1.27	+0.05/−1.10
H_{syn}-7	2.03	1.44	1.44	−0.59/0	1.85	1.39	1.27	−0.58/−0.12
H_{anti}-7	1.50	1.63	1.29	−0.21/−0.34	1.15	1.39	1.00	−0.15/−0.39
H_{syn}-8	5.12	5.33	4.25	−0.87/−1.08	5.14	5.17	4.00	−1.14/−1.17
H_{anti}-8	5.27	5.25	4.14	−1.13/−1.11	5.19	5.14	3.70	−1.49/−1.44
H-10/H-14	7.93	7.89	7.60	−0.33/−0.29	7.93	7.93	7.75	−0.18/−0.18
H-11/H-13	7.58	7.55	7.13	−0.45/−0.42	7.56	7.57	7.15	−0.41/−0.42
H-12	7.67	7.65	7.13	−0.54/−0.52	7.66	7.64	7.15	−0.51/−0.59
OCH_3	–	–	3.28	–	–	–	3.28	–
OCH_2	–	–	3.45/3.54		–	–	3.45/3.54	–

[a] $\Delta\delta_1 = \delta_{lithiosulfone} - \delta_{exo\ sulfone}$; $\Delta\delta_2 = \delta_{lithiosulfone} - \delta_{endo\ sulfone}$.

Table 3. ^{1}H-NMR data (*J* [Hz]) of sulfones *exo*-**5** and *endo*-**5** in $CDCl_3$ as well as of lithiosulfone **3** in $[D]_8$THF at 25°C

	exo-**5**	*endo*-**5**	**3**
H-1,H-2	0	2.2	–
H-1,H-4	1.5	1.5	1.6
H-1,H-5	0.5	0.8	0.8
H-1,H-6	3.1	2.7	2.4
H-1,H_{syn}-7	1.6	1.8	1.6
H-1,H_{anti}-7	1.6	1.8	1.9
H-1,H_{anti}-8	0.7	0.8	0
H-2,H_{anti}-7	1.6	0	–
H-2,H_{syn}-8	1.5	1.9	–
H-2,H_{anti}-8	1.6	2.2	–
H-4,H-5	3.1	3.2	3.1
H-4,H-6	0.5	0.5	0.5
H-4,H_{syn}-7	1.6	1.7	1.7
H-4,H_{anti}-7	1.6	1.7	1.7
H-5,H-6	5.5	5.5	5.1
H-5,H_{syn}-7	0.5	0.7	0.4
H-6,H_{syn}-7	0.5	0.7	0.4
H_{syn}-7,H_{anti}-7	9.0	8.7	6.2
H_{syn}-8,H_{anti}-8	0	0	2.7

2. Structure of the Lithiosulfones

a. Structure in the Crystal

Deprotonation of *exo*-**5**, *endo*-**5**, *endo*-**6** and *exo*-**6** with *n*PrLi in ether and recrystallization of the solids formed from diglyme gave the respective lithiosulfones **3** and **4** (each one containing a diglyme molecule per formula unit) in yields of 71% and 81%, respectively. X-ray structure analysis[21] revealed the heterochiral dimers *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme (Figures 4 and 5) whose Li atoms are bound to the sulfonyl O atoms but not to the allylic moieties, despite a favorable *s-cis* arrangement of the C2−S and the C3−C8 bonds.

The anions of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme both adopt a C2−S conformation in which the anionic lone pair orbital is periplanar to the S−Ph bond. X-ray crystal structure analysis of a number of lithiosulfones[11,16,25,26] had revealed similar dimeric O−Li contact ion pairs whose anions feature such a conformation, which is mainly due to a stabilizing hyperconjug-

Table 4. ^{13}C-NMR data (δ_C) of sulfones *exo*-**5**, *endo*-**5**, *exo*-**6** and *endo*-**6** in $CDCl_3$ as well as of lithiosulfones **3** and in $[D]_8$THF at 25°C

	exo-**5**	*endo*-**5**	**3**	$\Delta\delta_1/\Delta\delta_2$[a]	*exo*-**6**	*endo*-**6**	**4**	$\Delta\delta_1/\Delta\delta_2$[a]
C-1	45.7	45.4	49.1	+3.4/+3.7	40.2	40.5	43.9	+3.7/+3.4
C-2	67.4	68.9	70.7	+3.3/+1.8	70.7	69.4	72.5	+1.8/+3.1
C-3	142.8	143.1	154.0	+11.2/+10.9	146.6	146.0	156.8	+10.2/+10.8
C-4	50.6	52.3	57.2	+5.6/+4.9	45.1	47.0	51.6	+6.5/+5.6
C-5	139.9	135.0	130.9	−9.0/−4.1	29.6	28.1	30.5	+0.9/+2.4
C-6	135.6	133.0	137.7	+2.1/+4.7	28.3	22.8	31.7	+3.4/+8.9
C-7	46.3	49.8	54.9	+8.0/+5.1	35.8	39.0	42.7	+6.9/+3.7
C-8	111.1	109.9	83.8	−27.3/−26.1	110.0	108.4	77.3	−32.7/−31.1
C-9	139.0	139.4	149.4	+10.4/+10.0	138.8	140.2	150.9	+12.1/+10.7
C-10/C-14	128.8	128.6	125.1	−3.7/−3.5	128.9	128.2	124.7	−4.2/−3.5
C-11/C-13	129.2	129.2	127.9	−1.3/−1.3	128.9	129.2	128.1	−0.9/−1.1
C-12	133.7	133.6	128.6	−5.1/−5.0	133.4	133.5	128.6	−4.8/−4.9
OCH_3	–	–	59.0	–	–	–	59.0	–
OCH_2	–	–	71.3/72.9	–	–	–	71.1/72.9	–

[a] $\Delta\delta_1 = \delta_{lithiosulfone} - \delta_{exo\ sulfone}$; $\Delta\delta_2 = \delta_{lithiosulfone} - \delta_{endo\ sulfone}$.

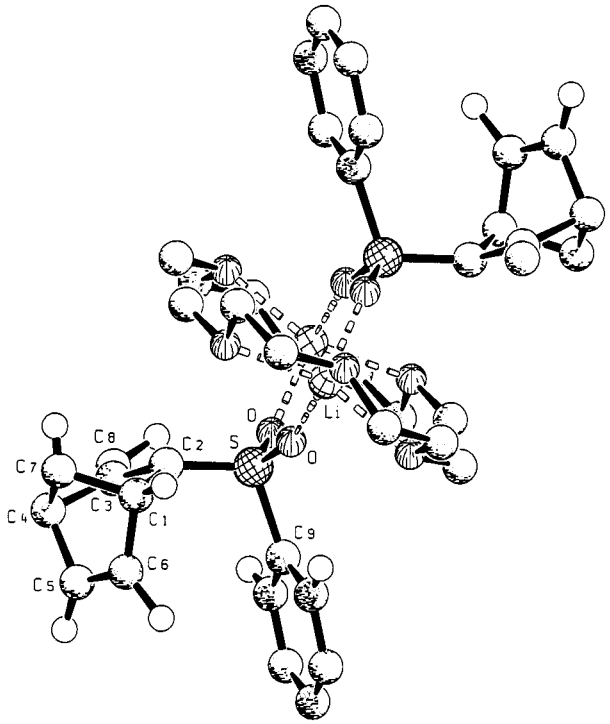


Figure 4. Crystal structure of *endo*-**3**/ent-*endo*-**3**·2diglyme

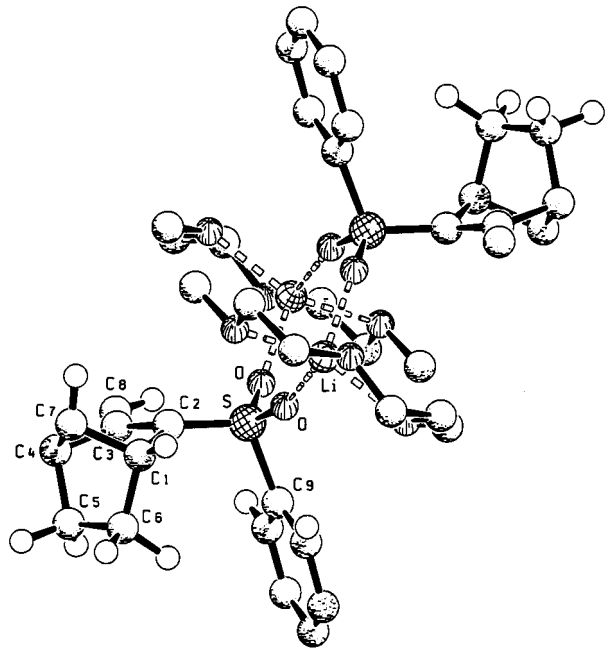


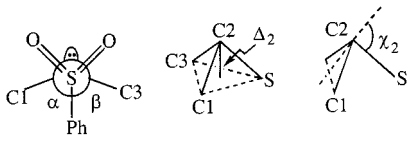
Figure 5. Crystal structure of *endo*-**4**/ent-*endo*-**4**·2diglyme

ative n_C-σ^*_{SR} interaction.[27] The phenyl groups of the anions of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme are both in the *endo* position.

A comparison of the bonding parameters of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme with those of the corresponding sulfones reveals a significant shortening of the C2−S and C2−C3 bonds and a less significant lengthening of the C3−C8 bond (cf. Table 1). The shortening of the C2−S bond is mainly caused by a Coulomb interaction between the negative charge at C2 and the positively charged S atom, as well as by a hyperconjugative n_C-σ^*_{SPh} interaction. According to experiment and theoretical calculations Coulomb interaction, hyperconjugation and polarization are the mechanisms (in this order) by which a sulfonyl group stabilizes a negative charge.[11,25−29] The shortening of the C2−C3 bond and the lengthening of the C3−C8 bond would be compatible with both an allylic delocalization of the negative charge and a Coulomb interaction stemming from a polarization of the C3−C8 double bond by the negative charge at C2 (vide infra).

The S atoms of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme are bent out of the C1−C2−C3 plane in the *endo* direction. Thus, the anionic C atoms (C2) of the two lithioallyl sulfones are not planar but pyramidalized in the *exo* direction, i. e., the apex of the pyramid at C2 points to the *exo* side, as indicated by several criteria of planarity (Table 5). The pyramidalization angle χ_2[30a] of the C2 atom of *endo*-**3**/ent-*endo*-**3**·2diglyme is 35.3(6)° and that of *endo*-**4**/ent-*endo*-**4**·2diglyme is 24.0(4)°. Such values correspond to a hybridization approximately half-way between sp^2 and sp^3.[31] The pyramidalization of C2 of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme is of the same magnitude as that found for the Cα atoms of $[(Me_2C-SO_2Ph)Li\cdot diglyme]_2$ (χ_α = 40.8°)[25b] and $(Me_2C-SO_2Ph)Li\cdot$[2.1.1]-cryptand (χ_α = 32.5°),[25e] whose anionic C atoms carry two methyl groups. In all of the aforementioned lithiosulfones the direction of pyramidalization of the anionic C atoms is the same, i. e., the apex of the pyramid at the anionic C atom is *syn* to the sulfonyl O atoms. According to experiment and theoretical calculation, the Cα atoms of non-planar α-sulfonyl carbanions feature such a direction of pyramidalization presumably because of the stabilizing hyperconjugative n_C-σ^*_{SPh} interaction and the minimization of torsional strain around the Cα−S bond.[11] One reason for the pyramidalization of the C2 atoms of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme is the minimization of strain energy in the bicyclic ring systems by the reduction of the C1−C2−C3 bond angle. The relief of torsional strain around the C2−S bond[25b,25e,25g] and of the allylic strain around the C2−C3 bond could also be important contributing factors.

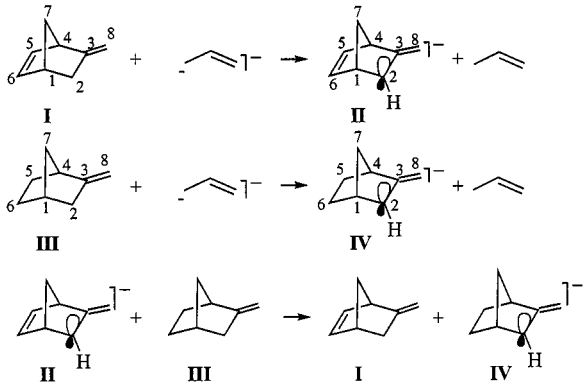
Table 5. Pyramidalization of the C2 atom in *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme



	endo-**3**	*endo*-**34**
Δ_2 [Å]	0.29	0.19
Σ_{C2} [°]	349.8	355.2
α [°]	67.2[a]	73.0[a]
β [°]	73.8[a]	79.5[a]
χ_2 [°]	35.3(6)[b]	24.0(4)[c]

[a] Absolute values. − [b] χ_2 = 180.0−144.7(6). − [c] χ_2 = 180.0−156.0(4).

Interestingly, the degree of pyramidalization of the C2 atom of the norbornyl species *endo*-**4**/ent-*endo*-**4**·2diglyme is less than that of the norbornenyl species *endo*-**3**/ent-*endo*-**3**·2diglyme. At first glance one is tempted to ascribe the greater planarization of the allylic moiety of the norbornyl anion *endo*-**4**/ent-*endo*-**4**·2diglyme to a steric interaction between the phenyl group and the H atoms 5-H_{endo} and 6-H_{endo}. However, the same direction and similar degrees of pyramidalization as for *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme were obtained when the structures of the free methylene norbornenyl anion **II** (χ_2 = 37.7°) and methylene norbornyl anion **IV** (χ_2 = 23.1°) (Scheme 2), formally derived from **3** and **4** by replacing the PhO_2S+Li group by a H atom, were optimized at the HF/6−31+G* level. When correlation energy (MP2) is included in additional single point calculations (MP2/6−31+G*//HF/6−31+G*) planarization of the allylic moiety in **II** requires 1.8 kcal/mol, indicating that the gain of allylic stabilization energy upon planarization is obviously insufficient to compensate for the presumed increase of strain energy. While the lengths of the C2−C3 and C3−C8 bonds are 1.413 Å and 1.370 Å in the pyramidalized species, their values change to 1.390 Å and 1.382 Å when the allylic moiety is planarized. These values are quite close to the length of the C−C bonds in the unsubstituted planar allyl anion which is 1.388 Å at the same level of theory. Intuitively, one expects that transfer of a negative unit charge from a planar allyl anion to an allylic moiety with a pyramidalized terminal C atom concurs with an increase of energy. The change of energy associated with the isodesmic reaction between the methylenenorbornene **I** and the unsubstituted allyl anion, however, reveals that this is not necessarily the case (cf. Scheme 2). While this energy of reaction is indeed positive at the HF/6−31+G*//HF/6−31+G* level (+5.1 kcal/mol), it is −1.9 kcal/mol when correlation energy is included in single point calculations. At −3.3 kcal/mol this change of energy is even more negative for the hypothetical reaction between the methylenenorbornane **III** and the unsubstituted planar allyl anion (cf. Scheme 2). This might at least in part be due to the fact that the degree of pyramidalization of the anionic center (C2) is lower in anion **IV** than in anion **II** and, therefore, allylic stabilization is more effective in this case. This is also reflected by the C2−C3 and C3−C8 bond lengths of **IV**, which are 1.397 Å and 1.383 Å and therefore much more similar to each other than the corresponding bond lengths in **II**. The relative stabilization of the negative charge in the anions of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme can be estimated approximately from the change of energy associated with the isodesmic reaction between **II** and **III** (cf. Scheme 2). This energy of reaction can be calculated from those associated with the other hypothetical reactions in Scheme 2, and amounts to −2.5 kcal/mol at the HF and −1.4 kcal/mol at the MP2/6−31+G*//HF/6−31+G* level. The significant reduction of this energy of reaction upon inclusion of MP2 corrections might indicate that a more complete treatment of the correlation energy will further reduce this value, and that stabilization of the negative charge is quite similar in both anions. This correlates well with measurements of the gas-phase acidities for the carbon acids **I** and **III** using the flowing afterglow technique, which revealed them to be the same.[33] In summary, the difference in the degree of Cα pyramidalization in *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme as well as **II** and **IV** is most likely due to the different ring strain of the norbornenyl and norbornyl ring systems.



Scheme 2. Isodesmic reactions of methylenenorbornene and methylenenorbornane with the allyl anion

It is of interest to note in context with the *exo* pyramidalization of the C2 atoms in the norbornenyl anion **II** and in the norbornyl anion **IV** that, according to experimental studies[30] and theoretical calculations,[34] in norbornene and its derivatives the C atoms of the double bond are also pyramidalized in the *exo* direction. This has been ascribed either to a minimization of the torsional strain around the two $C(sp^2)-C(sp^3)$ single bonds[30a,34b−d] or, alternatively, to the $\sigma_{C1\text{-}C6}$-π^* interaction being more stabilizing than the $\sigma_{C1\text{-}C7}$-π^* interaction.[30b,34e−k] Similarly, pyramidalization of the C2 atoms of **II** and **IV** in the *exo* rather than the *endo* direction (cf. Scheme 2) could be ascribed to a minimization of torsional strain around the C1−C2 bonds, or, alternatively to the hyperconjugative n_C-σ^*_{C1-C6} interaction being more stabilizing than the hyperconjugative n_C-σ^*_{C1-C7} interaction. An NBO analysis of the molecular wavefunctions of **II** and **IV** revealed that the n_C-σ^*_{C1-C6} interaction plays a much more important role in these anions than the n_C-σ^*_{C1-C7} interaction. However, working at the HF level, it has so far not been been possible to locate stationary points corresponding to those epimers of **II** and **IV** whose C2 atoms are pyramidalized in the *endo* direction. Changing the sign of the H−C2−C1−C3 dihedral angle and restarting the geometry optimization resulted in **II** and **IV**, respectively. Therefore single point calculations were performed for the starting geometries and the resulting wave-functions subjected to an NBO analysis. The results of these calculations show indeed that in the *endo* pyramidalized anions the n_C-σ^*_{C1-C7} interaction is more important than in the *exo* isomers while just the opposite is true for the interaction of the anionic lone pair with the σ^*_{C1-C6} orbital. However, since no stationary points for the *endo* anions could be located so far, it remains

uncertain whether the gain of stabilization energy due to increased n_C-σ^*_{C1-C7} mixing is sufficient to compensate the simultaneous loss of n_C-σ^*_{C1-C6} stabilization energy.

Finally, it seems to be of interest to compare the structures of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme with the crystal structure of the acyclic lithioallyl sulfone **7**/*ent*-**7**·2diglyme (Figure 6).[16] The structures of all three species are quite similar with respect to the coordination of the Li atom, the conformation of the anions, the degree of alternation of the bond lengths of the allylic moieties, the length of the bond between the S atom and the anionic C atom, and the direction of pyramidalization of the anionic C atoms. The degree of pyramidalization of the anionic C atom of the acyclic lithiosulfone, however, seems to be less than in the bicyclic lithiosulfones as expressed by $\chi_\alpha = 22.4°$. Interestingly, lithioallyl sulfoximines, the aza analogues of the sulfones, adopt a similar dimeric contact ion pair structure as *endo*-**3**/ent-*endo*-**3**·2diglyme, *endo*-**4**/ent-*endo*-**4**·2diglyme and **7**/*ent*-**7**·2diglyme in the crystal, being devoid of C−Li bonds.[35]

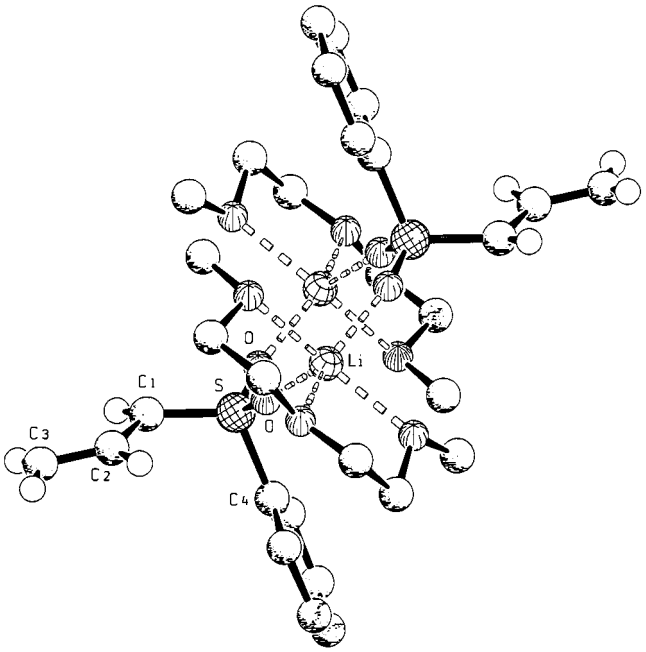


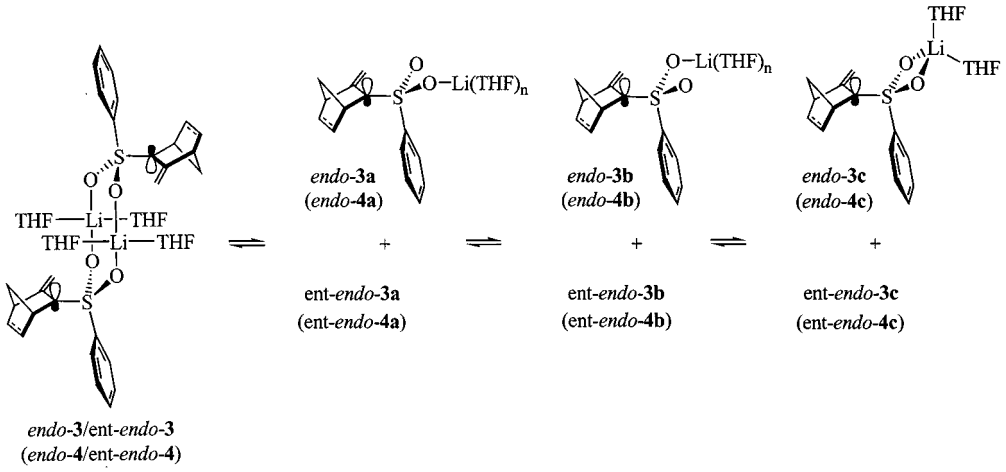
Figure 6. Crystal structure of **7**/*ent*-**7**·2diglyme; the view is constructed from the published coordinates;[16] selected bond lengths [Å]: S−C1 1.668(5), C1−C2 1.445(5), C2−C3 1.352(9)

b. Structure in Solution

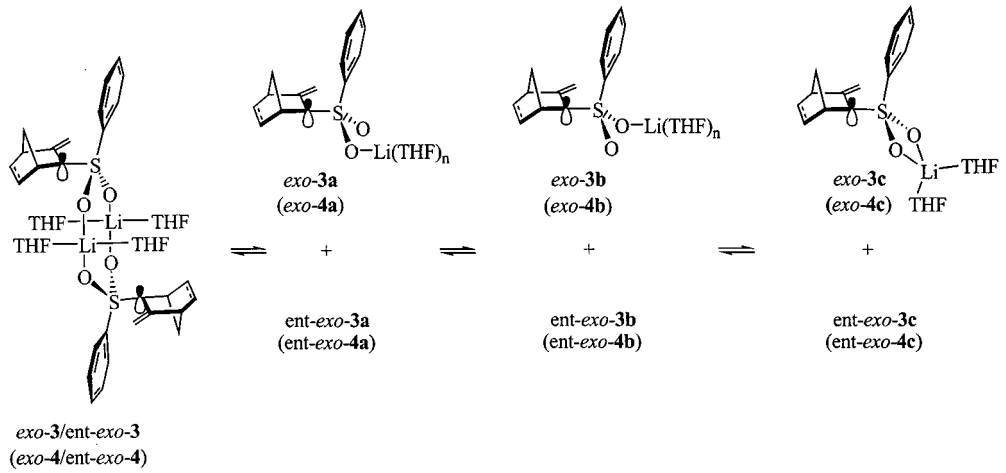
Acyclic lithiosulfones generally exist in THF solution as monomeric O−Li contact ion pairs being in equilibrium with small amounts of the corresponding dimeric O−Li contact ion pairs.[25c,25d,36−38] Because of the unknown aggregation of lithiosulfones of type **2**, that of **3** and **4** in THF by cryoscopy were determined.[39] Lithiosulfones **3** and **4** were prepared for the cryoscopic experiments by treatment of the corresponding sulfones *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6** with *n*BuLi in THF/*n*-hexane followed by removal of the solvents in vacuo. The microcrystalline lithiosulfones **3** and **4** thus prepared each contained two molecules of THF per formula unit according to ^{1}H-NMR spectroscopy. Aggregation states of $n = 1.58 \pm 0.13$ (c_{nom} = 49.7−50.3 mmol/kg) and of $n = 1.62 \pm 0.06$ (c_{nom} = 50.0−50.3 mmol/kg) were determined for the norbornenyl species **3** and the norbornyl species **4**, respectively, at the freezing point of THF (−108.5°C). Hence, at low temperatures in THF lithiosulfones **3** and **4** exist in this concentration range as approximately 1:1 mixtures of monomers and dimers (cf. Experimental Section). For the monomeric species the O−Li contact ion pair structures *endo*-**3a−c** (*endo*-**4a−c**) and *exo*-**3a−c** (*exo*-**4a−c**) can be envisioned, in which the Li atom is coordinated either by one or two O atom(s) and where the phenyl group is either *endo* or *exo* (Schemes 3 and 4).[12c] A contact ion pair structure of type *endo*-**3a**,**b** (*endo*-**4a**,**b**) and *exo*-**3a,b** (*exo*-**4a,b**) was found for 12-crown-4 complexed (α-benzyl)phenyl lithiobenzyl sulfone in the crystal,[40] while a contact ion pair structure of type *endo*-**3c** (*endo*-**4c**) and *exo*-**3c** (*exo*-**4c**) was discovered for 18-crown-6 complexed phenyl potassiobis(trimethylsilyl)-methyl sulfone and potassiomethyl tolyl sulfone in the crystal,[41][42] and located computationally for lithiomethyl methyl sulfone.[27b,27e] Likely structures for the dimeric O−Li contact ion pairs of **3** and **4** are *endo*-**3**/ent-*endo*-**3** (*endo*-**4**/ent-*endo*-**4**) and *exo*-**3**/ent-*exo*-**3** (*exo*-**4**/ent-*exo*-**4**), which are similar to those found in the crystal except for the replacement of the two diglyme molecules by four THF molecules. It was previously observed that the O−Li contact ion pair structure of a dimeric lithiosulfone in the crystal is basically not altered upon replacement of chelating ligands by THF molecules.[25c,25d] Based on this previous observation that aggregation has only a minor influence upon the anion structure of lithiosulfones,[25c,25d,27b,27e,40−42] the respective anions of monomers *endo*-**3a-c** (*endo*-**4a-c**) and *exo*-**3a-c** (*exo*-**4a-c**), as well as of dimers *endo*-**3**/ent-*endo*-**3** (*endo*-**4**/ent-*endo*-**4**) and *exo*-**3**/ent-*exo*-**3** (*exo*-**4**/ent-*exo*-**4**) are expected to exhibit basically the same structure.

In addition to the heterochiral dimers the corresponding homochiral dimers also have to be considered. In the crystal only dimers having *endo* anions were found. This may indicate that in solution dimers with *endo* anions are also more stable than those with *exo* anions (vide infra).

In order to gain further information about the monomer/dimer and, especially, *endo*/*exo* equilibria and as to the electronic structure of the allylic moieties of **3** and **4**, the lithiosulfones were studied by ^{1}H-, ^{13}C- and ^{6}Li-NMR spectroscopy. Lithiosulfones **3** and **4** were prepared for the spectroscopic investigations by the separate treatment of the respective sulfones *exo*-**5**, *endo*-**5**, *exo*-**6** and *endo*-**6** with *n*BuLi at −78°C in [D_8]THF, and ^{6}Li-labeled **3** and **4** were obtained by deprotonation of the corresponding sulfones with *n*Pr^{6}Li. Interestingly, the ^{1}H-NMR (400 MHz), ^{13}C-NMR (100 MHz) and ^{6}Li-NMR (44 MHz) spectra of **3** and **4** at −100°C in THF showed only one set of signals, together with only minor shift differences and line broadening. No differences in the NMR spectra of **3** and **4** were observed starting either from the corresponding *exo* or *endo* sulfone. Provided the respective monomeric and dimeric



Scheme 3. Monomer-dimer equilibria of the lithioallyl sulfones *endo*-**3** and *endo*-**4**



Scheme 4. Monomer-dimer equilibria of the lithioallyl sulfones *exo*-**3** and *exo*-**4**

contact ion pairs are NMR-spectroscopically distinguishable, these results indicate that attainment of the monomer/dimer and the *endo*/*exo* equilibria (vide infra) of **3** and **4** is fast on the NMR time scale at low temperatures (cf. Schemes 3 and 4). The *endo*/*exo* equilibration of **3** and **4** requires, besides other processes, C2−S bond rotation and C2 inversion. D-NMR spectroscopy of the lithium salts of chiral acyclic secondary α-phenylsulfonyl carbanions in $[D]_8$THF revealed $\Delta G^{\neq}$ values for their enantiomerization of 9−10 kcal/mol.[25c] Thus, in the case of **3** and **4** C2−S bond rotation and C2 inversion could have indeed such low barriers, allowing for a rapid equilibration of the *endo*/*exo* diastereomers at even −100°C.

The signals in the ^{1}H- and ^{13}C-NMR spectra of **3** and **4** at 25°C in $[D_8]$THF were completely assigned by a combination of NOE experiments and two-dimensional methods (H,H-COSY and C,H-COSY) (cf. Tables 2−4). An inspection of Tables 2 and 4 reveals that the changes occurring in the NMR spectra on going from the acid to the anion are, in both cases, similar in sign and magnitude.

^{6}Li,^{1}H-HOESY experiments[43] of **3** and **4** in $[D_8]$THF at −78°C revealed, on the average, close spatial proximities between the Li atom and the H atoms at C1, C8(H_{syn}) and those in the *ortho* position of the phenyl group for the monomers and dimers, having *endo* and *exo* anions. No NOE effect was observed, however, between the Li atom and the H atoms at C7(H_{syn}) and C6. The assumption of a close neighboring position of the Li atom and H-1 is corroborated by the downfield shift of the signal for H-1[43] of **3** and **4** as compared to sulfones *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6**, respectively. The results of the ^{6}Li{^{1}H}-NOE experiments would be compatible with both the *endo* species *endo*-**3a−c** (*endo*-**4a−c**) and *endo*-**3**/ent-*endo*-**3** (*endo*-**4**/ent-*endo*-**4**) as well as with the *exo* species *exo*-**3a−c** (*exo*-**4a−c**) and *exo*-**3**/ent-*exo*-**3** (*exo*-**4**/ent-*exo*-**4**) (cf. Figures 5 and 6). Thus, no statement as to the position of the *endo*/*exo* equilibria is possible. Somewhat more informative, however, were ^{1}H{^{1}H}-NOE experiments of **3** at 25°C in $[D_8]$THF, which revealed NOE effects only between the *ortho*-H atoms of the phenyl group and the H atoms at C6 and C8(H_{syn}), but not between the *ortho*-H atoms and the H atom at C7(H_{syn}). Unfortunately, similar ^{1}H{^{1}H}-NOE experiments were not possible in the case of **4** because of the almost identical chemical shifts for the H atoms at C6(H_{endo}) and C7(H_{syn}). These results might perhaps be taken as an indication for the *endo*/*exo* equilibria of **3** in THF, and most likely that of

4 also, being shifted to the side of the *endo* isomers (cf. Scheme 3).

Of particular interest is the mode of the additional stabilization of the negative charge of **3** and **4** provided by the neighboring double bond.[18] Chemical shift variations of the ^{13}C- and ^{1}H-NMR signals on going from the carbon acid to anion provide a good tool for an estimation of the structural changes occurring upon deprotonation and for the charge distribution in the anion.[28b] In case of **3** and **4** the situation is rather complex because of the existence of the monomeric and dimeric O−Li contact ion pairs having *exo* and *endo* anions. Because of the fast attainment of the various equilibria on the time scale of NMR spectroscopy, only averaged signals are observed. Thus, only a qualitative interpretation of the NMR data of **3** and **4** in regard to the above question is possible. An inspection of Tables 2 and 4 reveals the following shift variations (Δδ) on going from the respective sulfones *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6** to lithiosulfones **3** and **4**: (i) a slight downfield shift of the ^{13}C signal for C2, (ii) a strong upfield shift of the ^{13}C and ^{1}H signals for C8 and H-8, respectively, and (iii) a less strong downfield shift of the ^{13}C signal for C3. These shift variations correspond very well to those observed for other cyclic and acyclic lithiated allylic sulfones.[15−17,25g,44] It is generally accepted that two main effects, which oppose each other, contribute to the chemical shift variation of the ^{1}H- and ^{13}C-NMR signals on going from the carbon acid to the anion: an upfield shift due to the negative charge and a downfield shift in case of a change of the coordination geometry from tetrahedral to planar.[28] The shift variations recorded for the O−Li contact ion pairs **3** and **4** would thus be qualitatively compatible with allylic moieties which are characterized by (i) a coordination geometry of C2 between tetrahedral and planar, (ii) an accumulation of negative charge at C2 and C8 and (iii) an accumulation of positive charge at C3. In accordance with a degree of pyramidalization of the magnitude found in the crystal would also be the magnitude of the one-bond $^{13}C,^{13}C$ coupling between C2 and C3 and of the two-bond $^{13}C,^{13}C$ coupling between C2 and C9 through the SO_2 group[45] (Table 6).

Table 6. ^{13}C-NMR data (J [Hz]) of lithiosulfones **3** and **4** in $[D]_8$THF at 25°C

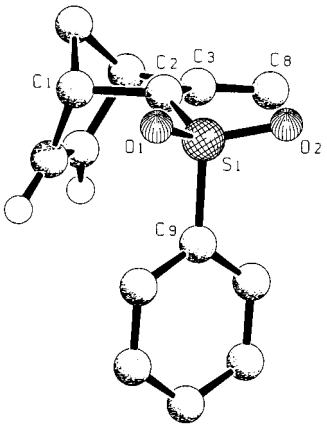
	3	**4**
C-1,C-2	35	40
C-1,C-6	36	33
C-1,C-7	31	30
C-2,C-3	62	55
C-2,C-9	−	9
C-3,C-4	34	37
C-3,C-8	76	75
C-4,C-5	36	31
C-4,C-7	31	30
C-5,C-6	70	31
C-9,C-10	−	57

The two mechanisms leading to a charge distribution of type $C2^{-}-C3^{+}-C8^{-}$ in **3** and **4** are allylic delocalization and/or polarization of the C3−C8 double bond by the negative charge at C2. The concept of a stabilization of allylic anions by resonance has been challenged recently on the basis of ab initio calculations.[32b] It was proposed that internal Coulomb interaction is the dominating mechanism of stabilization and that the contribution by resonance is only minimal. Stabilization of the anions of **3** and **4** by Coulomb interactions could indeed be important because of the existence of the extended charge alternating structure $O^{-}(O^{-})-S^{+}-C2^{-}-C3^{+}-C8^{-}$.[46] Quite interesting in regard to the question of the mode of the additional stabilization of the negative charge in **3** and **4** by the adjacent double bond is the observation that the $\Delta\delta_{8\text{-}H}$ and $\Delta\delta_{C8}$ values for the norbornyl species are significantly larger than those for the norbornenyl species (cf. Tables 2 and 4). This difference is most likely caused by a higher negative charge density at the C8 atom of **4** as compared to **3**. One of the main structural difference between *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme in the crystal is the higher degree of planarization of the allylic moiety of the norbornyl species. Since the accumulation of negative charge at C8 of **3** and **4** by allylic delocalization but not by polarization depends on the degree of planarization of the allylic moieties, the NMR data point to a significant allylic delocalization of the negative charge in **3** and **4**.

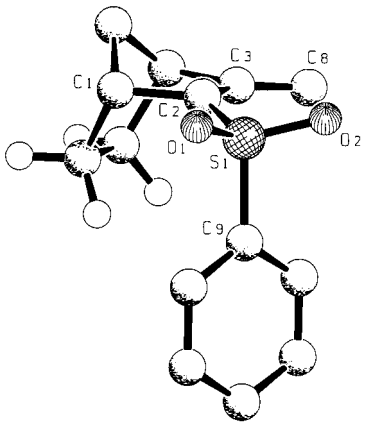
3. Structure of the Free Anions

The theoretical calculations of the free anions of **3** and **4** were carried out in order to obtain information as to the relative stabilities of the *endo* and *exo* conformers as well as to the distribution of their negative charge. In addition, structural information about the *exo* anions were sought because of their experimental inaccessibility. The structures of the *endo* and *exo* conformers of **3**($-Li^{+}$) and **4**($-Li^{+}$) have been optimized at the HF/6−31+G* level resulting in the local minima *endo*-**3**($-Li^{+}$), *exo*-**3**($-Li^{+}$), *endo*-**4**($-Li^{+}$) and *exo*-**4**($-Li^{+}$) (Figures 7 and 8, Table 7). The C2 atoms of *endo*-**3**($-Li^{+}$) and *endo*-**4**($-Li^{+}$) are pyramidalized into the *exo* direction as shown by the out-of-plane bending of the S atoms in the *endo* direction. The degree of pyramidalization is somewhat diminished as compared to that found in *endo*-**4**/ent-*endo*-**4**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme. The C2 atoms of the *exo* anions *exo*-**3**($-Li^{+}$) and *exo*-**4**($-Li^{+}$) are not planar but pyramidalized into the *endo* direction, and the degree of pyramidalization is similar to that of the *endo* anions *endo*-**3**($-Li^{+}$) and *endo*-**4**($-Li^{+}$). The agreement between the structural parameters of the free gas phase anions *endo*-**3**($-Li^{+}$) and *endo*-**4**($-Li^{+}$) and the anions of the dimeric contact ion pairs *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme in the crystal is reasonably good. According to the calculations the *endo* anions *endo*-**3**($-Li^{+}$) and *endo*-**4**($-Li^{+}$) are more stable than the *exo* anions *exo*-**3**($-Li^{+}$) and *exo*-**4**($-Li^{+}$) as expressed by their relative energies (MP2/6−31+G*//HF/6−31+G*) of +2.40 kcal/mol and +0.99 kcal/mol, respectively.

The distribution of the atomic point charges, which were calculated by the method of Kollman et al.,[47] in *endo*-

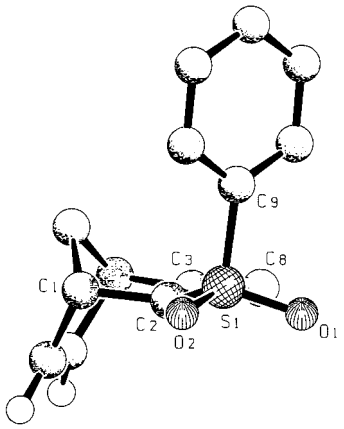


(a)

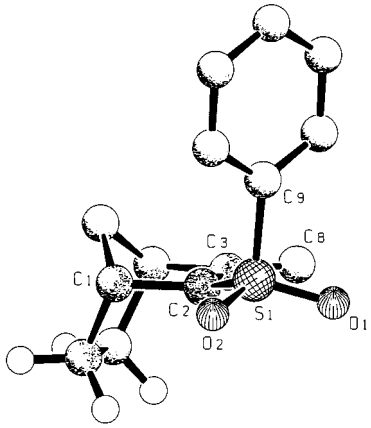


(b)

Figure 7. Calculated (HF/6−31+G*) structures of *endo*-**3**($-Li^+$) (a) and *endo*-**4**($-Li^+$) (b)



(a)



(b)

Figure 8. Calculated (HF/6−31+G*) structures of *exo*-**3**($-Li^+$) (a) and *exo*-**4**($-Li^+$) (b)

3($-Li^+$), *exo*-**3**($-Li^+$), *endo*-**4**($-Li^+$) and *exo*-**4**($-Li^+$) shows the pattern typical for the unsubstituted allyl anion,[32] i. e., negatively charged termini (C2, C8) and a positive charge at the central carbon atom (C3) whereby the negative charge is not equally distributed among C2 and C8. However, significant amounts of the negative charge are transferred onto the PhO_2S substituent, bonded to the C2−C3−C8$(H)_2$ segment.[48] While in the unsubstituted allyl anion the sum of the atomic charges of this segment amounts to −1.60 e, it is −0.72 e in *endo*-**3**($-Li^+$) and −0.70 e in *endo*-**4**($-Li^+$). The remaining negative charge in *endo*-**3**($-Li^+$) and in *endo*-**4**($-Li^+$) is transferred completely to the phenylsulfonyl group while those atoms of the norbornyl substituents which are not part of the allyl moiety result in very small positive charges of 0.03 e [*endo*-**4**($-Li^+$)] and 0.04 e [*endo*-**3**($-Li^+$)], respectively. No principal differences in the charge distribution of the *endo* and *exo* anions were found. Charge transfer from C2 to C8 in *endo*-**4**($-Li^+$) and *exo*-**4**($-Li^+$), whose allylic moieties are more planarized, is somewhat stronger than in *endo*-**3**($-Li^+$) and *exo*-**3**($-Li^+$). The C2−C3−C8 bond angles in all four anions cover the range between 134.1−134.6° and, therefore, are quite similar to the value for the free allyl anion (132.2°). The calculated charge distributions of the free anions are qualitatively in good agreement with those derived for the corresponding anions of the O−Li contact ion pairs by NMR spectroscopy (cf. Tables 2 and 4).

Table 7. Structural parameters and atomic charges of *endo*-**3**($-Li^+$), *endo*-**4**($-Li^+$), *exo*-**3**($-Li^+$) and *exo*-**4**($-Li^+$) at the HF/6−31+G* level

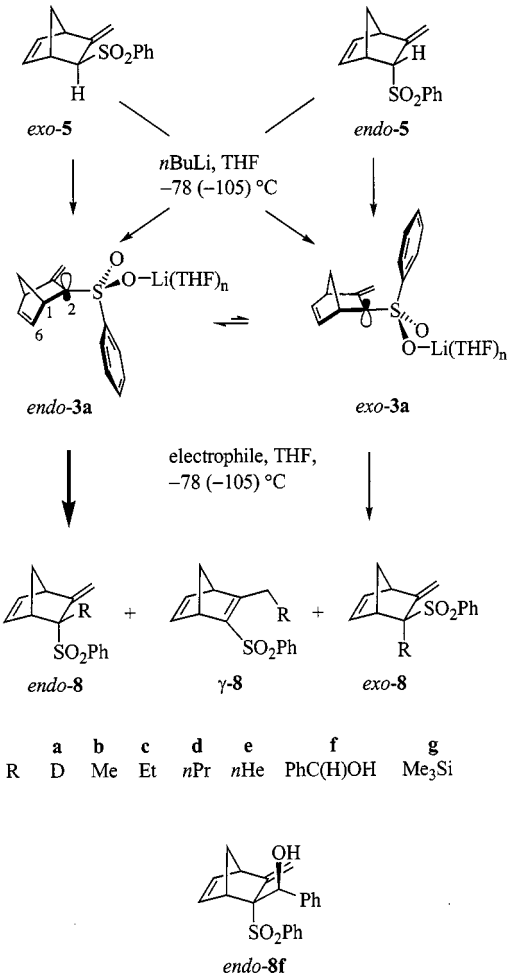
	endo-**3**($-Li^+$)	*endo*-**4**($-Li^+$)	*exo*-**3**($-Li^+$)	*exo*-**4**($-Li^+$)
S1−C2 [Å]	1.667	1.666	1.657	1.661
S1−C9 [Å]	1.808	1.808	1.809	1.807
S1−O1 [Å]	1.455	1.455	1.451	1.451
S1−O2 [Å]	1.451	1.451	1.455	1.455
C2−C3 [Å]	1.451	1.445	1.451	1.445
C3−C8 [Å]	1.343	1.346	1.342	1.346
Δ_2 [Å]	0.23	0.14	0.21	0.16
χ_2 [°]	26.6	17.0	24.2	18.5
q(C2) [e]	−0.70	−0.65	−0.50	−0.41
q(C3) [e]	+0.47	+0.48	+0.34	+0.30
q(C8) [e]	−1.02	−1.08	−0.98	−1.01
q(S) [e]	+1.10	+1.09	+0.98	+0.99
q(O1) [e]	−0.69	−0.67	−0.65	−0.66
q(O2) [e]	−0.69	−0.68	−0.68	−0.68

4. Reaction of the Lithiosulfones with Electrophiles

While alkylation of the norbornenyl anion **3** with MeI, allylic bromides and propargyl bromide had revealed the selective formation of the corresponding *endo* sulfones (87:13 to > 99:1 d.r.),[6e,6f] methylation of the norbornyl anion **4** with MeI was reported to give preferentially the corresponding *exo* sulfone (81:19 d.r.).[6e] No further reactions of **4** with electrophiles have been described, however. In the light of the results of the structural investigations of **3** and **4** outlined above and because of the questions elaborated upon in the introduction, it was decided to study their reaction with electrophiles on a broader basis. Especially reaction of **3** and **4** at low temperatures were sought starting separately from sulfones *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6** in the absence and in the presence of the electrophile (stepwise and in situ method, respectively).

a. Norbornenyl Anion

Deuteration of **3**, which was prepared by the separate treatment of *endo*-**5** and *exo*-**5** at −78°C with *n*BuLi in THF, with CF_3COOD at −78°C gave in both cases a mixture of *endo*-**8a** and *exo*-**8a** in a ratio of 87:13 (Scheme 5) (Table 8, entry 1). A similar result was obtained by using DCl instead of CF_3COOD under otherwise identical conditions (Table 8, entry 2). Reaction of **3** with MeI, EtI, *n*PrI and *n*HeI under the same conditions (stepwise method) afforded mixtures of *endo*-**8b−e** and *exo*-**8b−e**, in which the *endo* isomers dominated, in high yields (Table 8, entries 3−8). Selectivity of alkylation varied and was the highest in the case of the sterically more demanding alkylating reagents. No difference in the ratio of the methylation products *endo*-**8b** and *exo*-**8b** was observed by starting either from *endo*-**5** or *exo*-**5**.[6f,6g] The configurations of *exo*-**8b−e** and *endo*-**8b−e** were assigned unequivocally by NMR spectroscopy in combination with NOE experiments. Thus, the norbornenyl species **3** reacts with alkylating reagents, in accordance with previous observations,[6e,6f] under the preferential formation of the *endo* sulfones independent of the configuration of the starting sulfones. Hydroxyalkylation of **3** with PhCHO yielded different products depending on the reaction temperature (Table 8, entries 9 and 10). Thus, treatment of **3** with PhCHO at −78°C followed by addition of AcOH at −78°C shortly afterwards gave alcohols *endo*-**8f** and *exo*-**8f** in a ratio of 88:12 and none of alcohol γ-**8f**. Surprisingly, *endo*-**8f** and *exo*-**8f** were formed as single diastereomers. Normally, hydroxyalkylation of lithiosulfones proceeds with low diastereoselectivity.[13][14] While the configuration of *endo*-**8f** was secured by NOE experiments that of *exo*-**8f** has not been determined. Warming the reaction



Scheme 5. Reaction of the lithioallyl sulfone **3** with electrophiles

Table 8. Reaction of lithiosulfones **3** and **4** with electrophiles at −78°C in THF

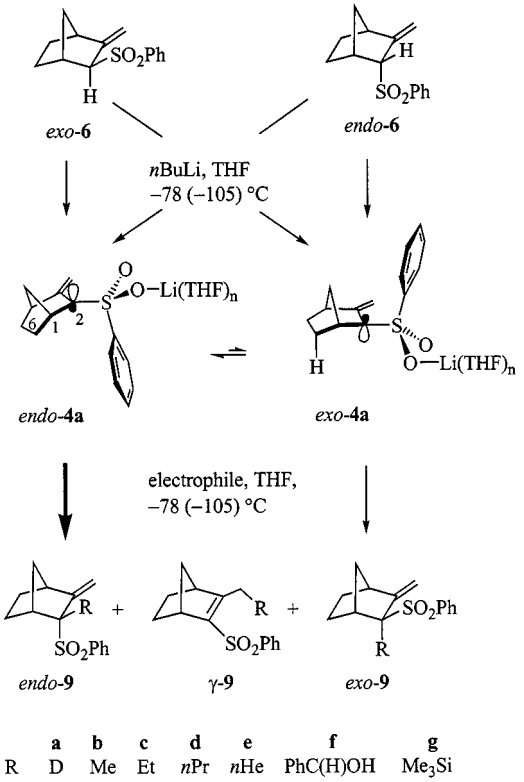
Electrophile	Entry	Product	R	*endo*/*exo*/γ	Yield (%)	Entry	Product	R	*endo*/*exo*/γ	Yield (%)
CF_3COOD	1	**8a**	D	87:13:0	95	12	**9a**	D	59:41:0	88
DCl	2	**8a**	D	88:12:0	91		–	–	–	–
MeI	3	**8b**[a]	Me	77:23:0	85	13	**9b**[b]	Me	81:19:0	90
MeI	4	**8b**[c]	Me	76:24:0	96	14	**9b**[d]	Me	80:20:0	90
MeI	5	**8b**[e]	Me	76:24:0	95	15	**9b**[f]	Me	80:20:0	87
EtI	6	**8c**	Et	83:17:0	84	16	**9c**	Et	95:5:0	91
*n*PrI	7	**8d**	*n*Pr	89:11:0	87	17	**9d**	*n*Pr	97:3:0	95
*n*HeI	8	**8e**	*n*Hex	88:12:0	80	18	**9e**	*n*He	97:3:0	81
PhCHO	9	**8f**	PhC(H)OH	88:12:0[g]	88	19	**9f**	PhC(H)OH	3:0:97[h]	79
PhCHO	10	**8f**[i]	PhC(H)OH	0:0:100[j]	72	20	**9f**[i]	PhC(H)OH	0:0:100[k]	66
Me_3SiCl	11	**8g**	Me_3Si	0:0:100	86	21	**9g**	Me_3Si	0:0:100	80

[a] From a mixture of *endo*-**5** and *exo*-**5**. – [b] From a mixture of *endo*-**6** and *exo*-**6**. – [c] From *endo*-**5**. – [d] From *endo*-**6**. – [e] From *exo*-**5**. – [f] From *exo*-**6**. – [g] Single diastereomers. – [h] 87:10 d.r. – [i] At 25°C. – [j] 50:50 d.r. – [k] 69:31 d.r.

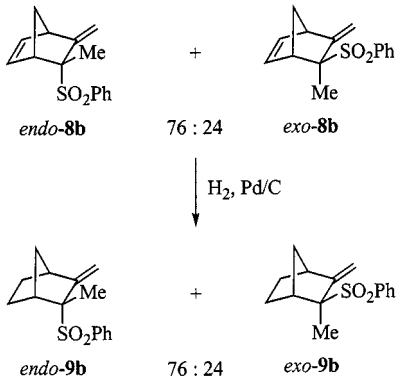
mixture derived from **3** and PhCHO to room temperature before quenching with aqueous $NaHCO_3$ led to isolation only of alcohol γ-**8f**. This temperature dependent reactivity of **3** towards PhCHO is typical for lithiated allylic sulfones which react with aldehydes under kinetic control in α position and under thermodynamic control in γ position.[13][14] Presumably because of steric reasons, reaction of **3** with Me_3SiCl occurred almost exclusively in γ position and gave γ-**8g** in 86% yield (Table 8, entry 11).

b. Norbornyl Anion

Deuteration of **4**, which was prepared by the separate treatment of *endo*-**6** and *exo*-**6** at −78°C with *n*BuLi in THF, with CF_3COOD at −78°C gave in both cases a mixture of *endo*-**9a** and *exo*-**9a** in a ratio of 59:41 (Scheme 6) (Table 8, entry 12). Reaction of **4**, which was prepared in the same manner as above, with MeI, EtI, *n*PrI and *n*HeI (stepwise method) proceeded in the same manner as that of **3** and gave preferentially the *endo* sulfones *endo*-**9b−e** (Table 8, entries 13−18). Here, too, selectivity of alkylation varied and was highest with the sterically more demanding alkylating reagents. We note that selectivities of alkylation of **4** were higher than those of **3**. Treatment of **4** with MeI in THF at −78°C afforded a mixture of *endo*-**9b** and *exo*-**9b** in a ratio of 80:20 (Table 8, entries 13−15) and not in an opposite ratio of 19:81 as reported previously.[6e,49] No difference in the ratio of the methylation products *endo*-**9b** and *exo*-**9b** was observed by starting either from *endo*-**6** or *exo*-**6**. The configurations of *endo*-**9b** and *exo*-**9b** were unequivocally determined by NMR spectroscopy in combination with NOE experiments. A final proof for the preferential formation of the *endo* sulfone *endo*-**9b** and not of the *exo* sulfone *exo*-**9b** in reaction of **4** with MeI was accomplished by chemical correlation (Scheme 7). Selective and partial hydrogenation of a 76:24 mixture of *endo*-**8b** and *exo*-**8b**[19] led to isolation of a 76:24 mixture of *endo*-**9b** and *exo*-**9b** in a yield of 86%.[50] Thus, the major isomer obtained by hydrogenation of the mixture of *endo*-**8b** and *exo*-**8b** and the major isomer formed in methylation of **4** are identical. Interestingly, reaction of **4** with PhCHO proceeded already at −78°C almost exclusively in γ position and gave alcohol γ-**9f** (Table 8, entries 19 and 20). The configurations of the other sulfones derived from **4** were also assigned by NMR spectroscopy in combination with NOE experiments. Presumably because of steric reasons, reaction of **4** with Me_3SiCl occurred almost exclusively in γ position and gave γ-**9g** in a yield of 80% (Table 7, entry 21).



Scheme 6. Reaction of the lithioallyl sulfone **4** with electrophiles



Scheme 7. Stereochemical correlation of the unsaturated sulfones *endo*-**8b**/*exo*-**8b** with the saturated sulfones *endo*-**9b**/*exo*-**9b**

c. In situ Methylation

Because of the fast isomerization of the *endo* and *exo* diastereomers of **3** and **4** even at −105°C, equilibria are fully established before addition of the electrophile occurs (stepwise method). Therefore the separate deprotonation of *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6** with *n*BuLi at low temperatures in the presence of MeI (in situ method) was studied. The in situ method has been successfully pioneered by Hoffmann et al. for the determination of the configurational stability of heteroatom-substituted chiral organolithium compounds.[51] Deprotonation of *endo*-**5** with *n*BuLi at −78°C in the presence of MeI (11 equiv.) led to isolation of a mixture of *endo*-**8b** and *exo*-**8b** in a ratio of 76:24, which is not different from that recorded by the stepwise method (Table 9, entry 1). However, deprotonation of *endo*-**5** with *n*BuLi at −105°C in the presence of MeI (11 equiv., c = 0.044 mol/L) led to isolation of a mixture of sulfones *endo*-**8b** and *exo*-**8b** in a ratio of 68:32 (Table 9, entry 2). The ratio of *endo*-**8b** and *exo*-**8b** changed even to 61:39 (Table 9, entry 3) by raising the amount of MeI in the in situ methylation to 100 equiv. (c = 4.0 mol/L) under otherwise identical conditions. In a control experiment *endo*-**5** was treated with *n*BuLi at −78°C followed by addition of MeI at −105°C to give a mixture of *endo*-**8b** and

Table 9. In situ methylation of sulfones *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6**

Entry	Sulfone	Lithiosulfone	*T* [°C]	Equiv. MeI	Product	*endo*/*exo*	Yield (%)
1	*endo*-**5**	**3**	−78	11	**8b**	76:24	96
2	*endo*-**5**	**3**	−105	11	**8b**	68:32	98
3	*endo*-**5**	**3**	−105	100	**8b**	61:39	96
4	*endo*-**5**	**3**	−105[a]	11	**8b**	76:24	96
5	*exo*-**5**	**3**	−78	11	**8b**	65:35	96
6	*exo*-**5**	**3**	−105	11	**8b**	57:43	98
7	*exo*-**5**	**3**	−105	100	**8b**	45:55	98
8	*exo*-**6**	**4**	−78	11	**9b**	80:20	99
9	*exo*-**6**	**4**	−105	11	**9b**	81:19	99
10	*endo*-**6**	**4**	−105	11	**9b**	80:20	99

[a] Deprotonation at −78°C and addition of MeI at −105°C after 20 min.

exo-**8b** in the same ratio (Table 9, entry 4) as recorded by the stepwise method at −78°C. Thus, the differences observed in the stepwise and the in situ methylation of the norbornenyl sulfone *endo*-**5** can not be due to a temperature dependency of the diastereoselectivity of the methylation or of the equilibria between the various contact ion pairs. Rather, the lower diastereomer ratios of sulfones *endo*-**8b** and *exo*-**8b** obtained by the in situ method, especially at a higher concentration of MeI, indicate that the trapping of the *endo* and *exo* anionic species now competes more with their isomerization. The in situ methylation of the *exo* norbornenyl sulfone *exo*-**5** took a similar course but resulted in an inversion of the ratio of *endo*-**8b** and *exo*-**8b** (Table 9, entries 5−7). Whereas the stepwise methylation of *exo*-**5** at −78°C gave *endo*-**8b** and *exo*-**8b** in a ratio of 76:24, its in situ methylation at −105°C yielded the two sulfones in a ratio of 45:55. These results strongly support the notion that **3** forms an equilibrium mixture of *endo*-**3** and *exo*-**3** in THF solution (vide infra). In contrast to the in situ methylation of the norbornenyl sulfones that of the norbornyl sulfones *exo*-**6** and *endo*-**6** revealed no differences as compared to the stepwise method at −78°C (Table 9, entries 8−10). At a first glance it seems odd that only the in situ methylation of *endo*-**5** and *exo*-**5** gives different product ratios upon lowering the temperature from −78°C to −105°C or by raising the concentration of MeI. We have observed, however, that during the dropwise addition of *n*BuLi to a mixture of *exo*-**6** or *endo*-**6** and MeI (11 equiv.) at −105°C in THF a transient yellow color developed whereas in the case of the similar in situ methylation of *exo*-**5** or *endo*-**5** no such phenomenon was observed. Since formation of **3** and **4** is associated with the development of an intensive yellow color of their solutions, this indicates that the norbornyl species **4** has a lower reactivity towards MeI than the norbornenyl species **3** and, as a consequence, the *endo*/*exo* equilibrium of **4** is presumably fully attained before methylation occurs even in the presence of the electrophile.

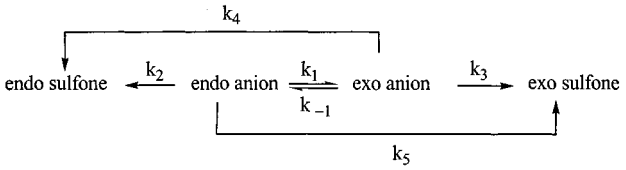
d. Model for the *endo*/*exo* Selectivity of Anion Reaction

According to the aforementioned results, the *endo* and *exo* diastereomers of **3** and **4** are conformationally labile on the time scale defined by the rate of their reaction with electrophiles. Hence, the Curtin-Hammett/Winstein-Holness concepts[52] should apply to the *endo*/*exo* selectivity of reaction of **3** and **4** with electrophiles. Before an attempt is made to rationalize the stereoselectivity three questions have to be addressed. (1) What are the reactive species? (2) What is the stereoselectivity of their reaction with electrophiles? (3) Although of less importance in the present case, what is the stereoselectivity of the deprotonation of the *endo* and *exo* isomers of **5** and **6**? In THF solution the respective monomeric contact ion pairs *endo*-**3a−c** (*endo*-**4a−c**) and *exo*-**3a−c** (*exo*-**4a−c**) as well as the corresponding homo- and heterochiral dimers have to be considered primarily as reactive species (cf. Schemes 3 and 4). An inspection of space-filling models of monomers *endo*-**3c** (*endo*-**4c**) and *exo*-**3c** (*exo*-**4c**) as well as of dimers *endo*-**3**/ent-*endo*-**3** (*endo*-**4**/ent-*endo*-**4**) and *exo*-**3**/ent-*exo*-**3** (*exo*-**4**/ent-*exo*-**4**) shows, however, that their anionic C atoms ought to be severely shielded by the THF molecule(s) in the *syn* position. Thus, more likely candidates should be the monomers *endo*-**3a**,**b** (*endo*-**4a**,**b**) and *exo*-**3a**,**b** (*exo*-**4a**,**b**) in which the C2 atom is less shielded by the THF solvated Li atom. It should be noted, however, that *endo*-**3c** (*endo*-**4c**) and *exo*-**3c** (*exo*-**4c**) might be in equilibrium with the corresponding mono-solvated species whose C2 atom is less shielded towards electrophiles. Although it has been concluded from determination of ion pair acidities and conductivities that lithiosulfones are O−Li contact ion pairs (CIP) in THF,[38] the existence of minute amounts of solvent separated ion pairs (SSIP), which might have a higher reactivity than CIPs, cannot be excluded. However, based on X-ray crystallography of lithium and tetrabutyl ammonium salts of α-sulfonyl carbanions[25c,25d] it can be safely assumed that the anions of the corresponding CIPs and SSIPs will have similar structures.[11,25−27]

A study of the reactivity of conformationally stable acyclic chiral *S*-*tert*-butyl- and *S*-trifluoromethylsulfonyl carbanions had revealed a very high propensity for electrophiles to attack the anionic C atom, irrespective of its coordination geometry, syn to the O atoms and, thus, anti to the *tert*-butyl and trifluoromethyl groups.[25f,53] This has been attributed to a shielding of the face of the anionic C atom anti to the O atoms by the substituent at the S atom. In addition a possible energy lowering interaction between the electrophile and the Li atom, which is coordinated to the O

atom of the sulfonyl group, may contribute to the high *syn* selectivity, too. Thus, because of similar parameters for the freely rotating phenyl group ($E_s = 1.01_{depth}$, $E_s = 3.82_{width}$), the *t*Bu group ($E_s = 2.78$) and the CF_3 group ($E_s = 2.4$),[54] it is believed that *endo* attack on *endo*-**3a,b** (*endo*-**4a,b**) and *exo* attack on *exo*-**3a,b** (*exo*-**4a,b**) are sterically hindered and that electrophiles attack *endo*-**3a,b** (*endo*-**4a,b**) with a high preference at the *exo* face and *exo*-**3a,b** (*exo*-**4a,b**) at the *endo* face (cf. Schemes 3 and 4). The *exo* attack on *endo*-**3a,b** and *endo*-**4a,b** should be likewise preferred because of the pyramidalization of the anionic C atoms[55][56] in the *exo* direction. Unfortunately, experimental information as to the coordination geometry of the C2 atom of the *exo* anions *exo*-**3a-c**, *exo*-**4a-c**, *exo*-**3**/ent-*exo*-**3** and *exo*-**4**/ent-*exo*-**4** is not available. However, the ab initio calculation of the free *exo* anions *exo*-**3**(−Li+) and *exo*-**4**($-Li^+$) have revealed a pyramidalization of C2 in the *endo* direction which is of the same magnitude as found in *endo*-**3**($-Li^+$) and *endo*-**4**($-Li^+$). Thus, it seems safe to assume that the C2 atoms of *exo*-**3a−c**, *exo*-**4a−c**, *exo*-**3**/ent-*exo*-**3** and *exo*-**4**/ent-*exo*-**4** are pyramidalized in the *endo* direction. This should provide an additional bias for a preferential attack of electrophiles on *exo*-**3a−c**, *exo*-**4a−c**, *exo*-**3**/ent-*exo*-**3** and *exo*-**4**/ent-*exo*-**4** at the *endo* face.

On the basis of the above assumptions the preferential formation of *endo*-**8a−f** (*endo*-**9a−e**) in reaction of **3** (**4**) is ascribed to the *exo* attack of the electrophiles on *endo*-**3a,b** (*endo*-**4a,b**) being faster than *endo* attack on *exo*-**3a,b** (*exo*-**4a,b**) in combination with the *endo*/*exo* equilibration of the anionic species being faster than their reaction with the electrophiles (cf. Schemes 5 and 6). The underlying kinetic scheme is depicted in Scheme 8.[57] It should be emphasized, however, that this scheme represents an oversimplification since other possibly reacting species have not been considered and because of the limiting assumptions which have been made above.



Scheme 8. Simplified kinetic scheme for the reaction of the *endo* and *exo* conformers of carbanions **3** and **4** with electrophiles

Now the question has to be addressed as to why *endo*-**3a,b** (*endo*-**4a,b**) should be more reactive towards electrophiles than *exo*-**3a,b** (*exo*-**4a,b**). It has long been recognized that the *exo* attack of electrophiles on norbornenes[58] is preferred over the *endo* attack. Several explanations for the *exo* preference such as the torsional effect, the *exo* pyramidalization, the *endo* deformability and the staggering effect have been advanced.[30a,34c−34e,34h,34i,59] According to Houk's staggering effect, the *exo* attack on norbornene is preferred over the *endo* attack because in the transition state of the *exo* attack the developing C2−R bond and the C1−C6 bond are nearly ideal staggered whereas in the transition state of the *endo* attack these bonds are more eclipsing.[34c,34d] Thus, the *exo* attack of electrophiles on *endo*-**3a,b** (*endo*-**4a,b**) should be faster than the *endo* attack on *exo*-**3a,b** (*exo*-**4a,b**) because in the transition state of the *exo* attack on *endo*-**3a,b** (*endo*-**4a,b**) the developing C2−R bond and the C1−C6 bond are nearly staggered whereas in the transition state of *endo* attack on *exo*-**3a** (*exo*-**4a**) those bonds are eclipsed (Figure 9). In an alternative but closely related view the faster *exo* attack on *endo*-**3a,b** (*endo*-**4a,b**) can be ascribed to the developing C2−R bond and the C1−C7 bond in the transition state of the *exo* attack on *endo*-**3a,b** (*endo*-**4a,b**) being less eclipsing than the developing C2−R bond and the C1−C6 bond in the transition state of *endo* attack on *exo*-**3a** (*exo*-**4a**). It should be

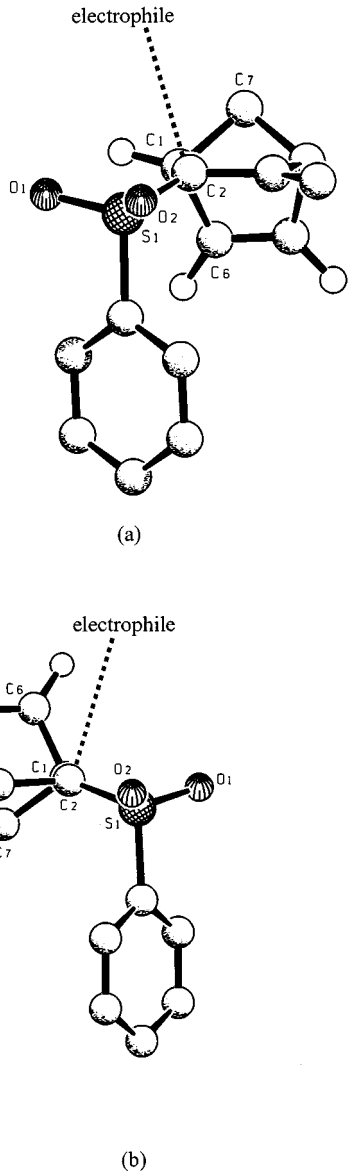


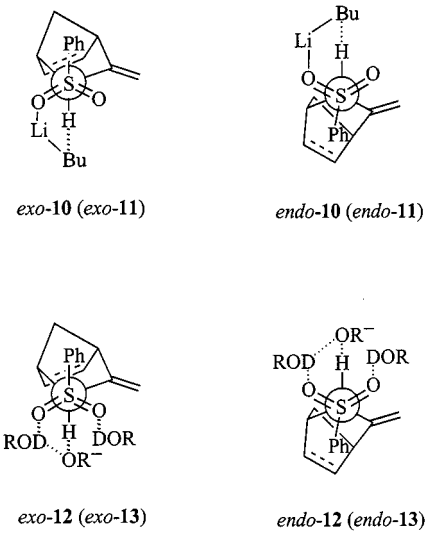
Figure 9. Modell for the trajectory of attack of electrophiles on the *exo* face of *endo*-**3**($-Li^+$) (a) and on the *endo* face of *exo*-**3**($-Li^+$) (b); the views are constructed from the calculated coordinates of *endo*-**3**($-Li^+$) and *exo*-**3**($-Li^+$) by picturing the trajectory manually

emphasized, however, that although the staggering effect offers a rationalization for the selectivity of reaction of **3** and **4** with electrophiles, it may well be that other not yet revealed factors are contributing, too.

The higher selectivities of alkylation of **4** as compared to **3** could be ascribed within this scheme to the *endo* attack on *exo*-**4a** being even further disfavored as compared to the *exo* attack on *endo*-**4a** because of a shielding of the *endo* face of the C2 atom in *exo*-**4a** by 6-H_{endo} (cf. Scheme 6).[1c] Finally, it is tempting to ascribe the higher reactivity of the norbornenyl species **3** as compared to the norbornyl species **4** in alkylation to the higher degree of the pyramidalization of its C2 atom (vide supra).

e. H/D Exchange of the Sulfones

Although the *endo*/*exo* selectivities of deprotonation of sulfones *exo*-**5**, *endo*-**5**, *endo*-**6** and *exo*-**6** with *n*BuLi should have only little bearing upon the selectivity of reaction of **3** and **4** with electrophiles, their knowledge would, nevertheless, be of interest. It had been observed previously that deprotonation of chiral acyclic *tert*-butyl and trifluoromethyl sulfones with organolithium compounds generally occurs with high selectivity apparently in a Cα−S conformation in which the α-H atom is gauche to both O atoms.[25f,53] This was rationalized on the basis of an intramolecular deprotonation following complexation of RLi by the sulfonyl O atom[60] in combination with a preferred Cα−S conformation resembling that of the α-sulfonyl carbanion formed. Thus in the case of sulfones *exo*-**5** (*exo*-**6**) and *endo*-**5** (*endo*-**6**) transition states of type *exo*-**10** (*exo*-**11**) and *endo*-**10** (*endo*-**11**) (Scheme 9), respectively, would have to be considered. However, judged by molecular models these transition states appear to be less likely because of a steric interaction between the phenyl group and the methylene (C7) and ethano/etheno (C5, C6) bridges, respectively. This seemed to be an especially serious argument if one considers that in the transition state of sulfone deprotonation only a minor structural reorganization occurs.[64][65] Cram et al.,[61] Corey et al.[62] and Goering et al.[63] had studied the H/D exchange of optically active acyclic sulfones with alkoxides in deuterated alcohols and observed a high degree of retention of configuration. This observation was rationalized by proposing a retention mechanism which features (i) an intramolecular deprotonation of the sulfone in a conformation in which the H atom is gauche to both O atoms following a coordination of the base and the deuterated solvent molecules to the O atoms, and (ii) an intramolecular transfer of a D atom *syn* to the O atoms before Cα−S rotation and, thus, racemization can take place. It was thus of interest to determine the stereochemistry of the H/D exchange of sulfones *exo*-**5**, *endo*-**5**, *endo*-**6** and *exo*-**6** in order to obtain information as to the likelihood of transition states of deprotonation, featuring a C2−S conformation in which the 2-H atom bisects the O−S−O angle. Treatment of the norbornenyl sulfone *endo*-**5** with 2.5 mol-% $NaOCD_3$ in CD_3OD at 25°C led, after a reaction time of 4.5 h, to isolation of a mixture of 64% *endo*-**5** and 36% *endo*-**8a** containing none of the *exo* isomer *exo*-**8a** (Table 10). In a similar experiment *exo*-**5** was treated with 2.5 mol-% $NaOCD_3$ in CD_3OD to give, after a reaction time of 21 h, a mixture of 42% *exo*-**5** and 58% *exo*-**8a** uncontaminated by the *endo* isomer *endo*-**8a** (Table 11). In both cases a mixture of *exo*-**8a** and *endo*-**8a** in a ratio of 76:24 was obtained after a prolonged reaction time of 56.5 h. Similar observations were made in the case of the H/D exchange of the norbornyl sulfones *endo*-**6** and *exo*-**6**. While the *endo* sulfone *endo*-**6** gave after a reaction time of 8 h a mixture of 31% *endo*-**6** and 69% *endo*-**9a** and none of *exo*-**9a** (Table 12), the *exo* sulfone *exo*-**6** yielded, after a reaction time of 29 h, a mixture of 49% *exo*-**6** and 51% *exo*-**9a** uncontaminated by *endo*-**9a** (Table 13). In both cases the equilibrium mixture contained *exo*-**9a** and *endo*-**9a** in a ratio of 86:14. These results show, that the base-catalyzed H/D exchange of *endo*-**5**, *exo*-**5**, *endo*-**6** and *exo*-**6**, which is faster than diastereomerization, takes place under a high degree of retention of configuration. Thus, at least under

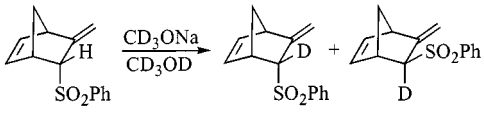


exo-**10** (*exo*-**11**) *endo*-**10** (*endo*-**11**)

exo-**12** (*exo*-**13**) *endo*-**12** (*endo*-**13**)

Scheme 9. Transition state models for the base-catalyzed H/D exchange of sulfones *exo*-**5**, *endo*-**5**, and *exo*-**6**

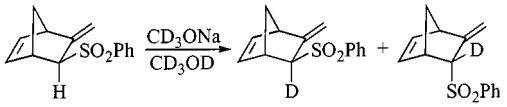
Table 10. H/D-Exchange of sulfone *endo*-**5**



endo-**5** *endo*-**8a** *exo*-**8a**

t [h]	*endo*-**5** (%)	*endo*-**8a** (%)	*exo*-**8a** (%)
0	100	–	–
0.67	100	–	–
2.5	93	7	–
4.5	64	36	–
12	13	78	9
21	–	82	18
27.5	–	62	38
36	–	39	61
43	–	31	69
46.5	–	29	71
56.5	–	24	76

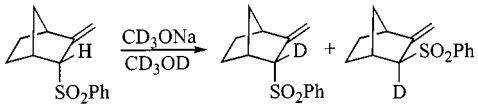
Table 11. H/D-Exchange of sulfone *exo*-**5**



exo-**5** *exo*-**8a** *endo*-**8a**

t [h]	*exo*-**5** (%)	*exo*-**8a** (%)	*endo*-**8a** (%)
0	100	–	–
1	98	2	–
3	91	9	–
4.5	89	11	–
12.5	66	34	–
21	42	58	–
27.5	4	83	13
36	–	79	21
43	–	78	22
56.5	–	76	24

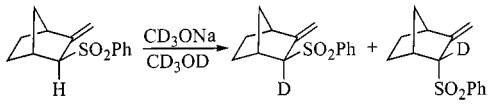
Table 12. H/D-Exchange of sulfone *endo*-**6**



endo-**6** *endo*-**9a** *exo*-**9a**

t [h]	*endo*-**6** (%)	*endo*-**9a** (%)	*exo*-**9a** (%)
0	100	–	–
0.33	98	2	–
1.75	81	19	–
3	59	41	–
5	45	55	–
8	31	69	–
14.5	10	80	10
24	–	83	17
28.5	–	77	23
39.5	–	64	36
65	–	33	67
72	–	28	72
91.5	–	14	86

Table 13. H/D-Exchange of sulfone *exo*-**6**



exo-**6** *exo*-**9a** *endo*-**9a**

t [h]	*exo*-**6** (%)	*exo*-**9a** (%)	*endo*-**9a** (%)
0	100	–	–
0.67	98	2	–
2	95	5	–
8	93	7	–
15	80	20	–
24.5	59	41	–
29	49	51	–
39.5	28	65	7
65.5	4	84	12
72	–	86	14

the conditions employed, the attainment of transition states of deprotonation of type *exo*-**12** (*exo*-**13**) and *endo*-**12** (*endo*-**13**), in which the H-2 atom bisects the O−S−O angle, seems feasible.

Conclusion

The lithioallyl sulfones **3**, **4**, and **7** crystallize preferentially as dimeric contact ion pairs whose Li atoms are coordinated to the O atoms and not to the allylic moieties, despite a favorable arrangement of the allylic moiety and the sulfonyl group in the first two cases. This is in sharp contrast to the known crystal structures of other heteroatom-substituted allyllithium compounds, where the Li atoms make contact, not only to the heteroatoms, but also to the allylic moieties.[66] The anions of the three lithioallyl sulfones adopt the typical Cα−S conformation of α-sulfonyl carbanions and feature reduced Cα−S bond lengths. Their allylic moieties are characterized by non-planar anionic C atoms and by bond alternation. The degree of pyramidalization corresponds to a hybridization approximately halfway between sp^2 and sp^3 and the direction of pyramidalization is such that the apex of the pyramid at Cα is *syn* to the O atoms. In the crystal both anions of **3** and **4** prefer the *endo* conformation and possess in the *exo* direction pyramidalized anionic C atoms. The C2 atoms of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme show a different degree and the same direction of pyramidalization which points to a minimization of strain energy as the common cause for this difference. This is supported by the ab initio calculations of the parent anions **II** and **IV**. The crystallographic results are nicely corroborated by the ab initio calculation of the free anions *endo*-**3**(−Li^+), *exo*-**3**(−Li^+), *endo*-**4**(−Li^+) and *exo*-**4**(−Li^+), which revealed similar degrees but opposite directions of the pyramidalization of the C2 atoms.

In THF solution the structural picture of **3** and **4** is much more complex. Monomeric and dimeric O−Li contact ion pairs, having *endo* and *exo* anions, are in rapid equilibrium, even at low temperatures, whereby the *endo* species seem to be the preferred one. This is supported by the ab initio calculations of the free anions which revealed small energy differences in favor of the *endo* isomers. Based on the NMR data the extra stabilization of the negative charge of **3** and **4** by the double bond seems to be due to allylic delocalization. However, because of the charge-alternating structure O^-−$(O^-)S^+$−$C2^-$−$C3^+$−$C8^-$, internal Coulomb interaction may provide an additional and important stabilization. Such charge-alternating structures were also located by the ab initio calculations of *endo*-**3**(−Li^+) and *endo*-**4**(−Li^+), *exo*-**3**(−Li^+) and *exo*-**4**(−Li^+).

Both lithiosulfones **3** and **4** react with electrophiles with high selectivities under formation of the corresponding *endo*-sulfones. Thus, the previous report on a selective *endo*-methylation of **4**[6e] has to be revised. The similar *endo*/*exo* selectivities of reaction of **3** and **4** with electrophiles can be rationalized by assuming that (i) *endo* and *exo* species are

configurationally labile on the time scale defined by the rate of reaction with electrophiles, (ii) *endo* anions react with electrophiles highly selective from the *exo* side and *exo* anions from the *endo* side, and (iii) *endo* anions are more reactive than *exo* anions. It will be interesting to see whether the replacement of the phenyl group in **3** and **4** by a *tert*-butyl group will lead, as in other cases, to anions which are conformationally stable on the time scale defined by the rate of their reaction with electrophiles.

Experimental Section

Computational Methods: The geometries of the anions were optimized at the HF level of ab initio theory employing the 6−31+G* basis set,[67][68] while the 6−31G* set of gaussians was used for the sulfones.[69−72] In order to include correlation energy single point calculations at the HF/6−31+G*- and HF/G-31G*-optimized structures using Møller-Plesset perturbation theory[73] to the second order (MP2/basis set//HF/basis set) were performed. All ab initio calculations were carried out employing the GAUSSIAN 94 set of quantum chemical routines[74] running on an SNI-s600/20 computer of the Rechenzentrum at the RWTH Aachen.

X-ray Analyses: Suitable single crystals of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme were sealed in capillary tubes. The crystal data and the most salient experimental parameters used in the X-ray measurements and in the crystal structure analyses are reported in Tables 14 and 15. The crystal structures of *endo*-**5**, *exo*-**5** and *endo*-**6** were solved using direct methods as implemented in the XTAL3.2 package of crystallographic routines,[75] employing GENSIN[76] to generate structure-invariant relationships and GENTAN[77] for the general tangent phasing procedure. The crystal structures of *endo*-**3**/ent-*endo*-**3**·2diglyme and *endo*-**4**/ent-*endo*-**4**·2diglyme were solved by direct methods and refined using SHELX-97.[78] Experimental and theoretical molecular structures were visualized with the program SCHAKAL 92.[79]

Cryoscopy: The cryoscopic experiments were carried out according to Bauer and Seebach.[39] Temperature measurements were made by using a Pt 100 platin thermo-couple of type 42943 (Burster Präzisionsmeßtechnik, Gensbach) in connection with a high-precision thermometer Kelvimat Typ 4321 (Burster Präzisionsmeßtechnik, Gensbach) (± 0.002 K). Every 3 s the temperature was registrated by a personal computer. For the measurements, the solution of the lithiosulfone was filled with a double-ended needle into the cryoscopic vessel up to a gauge mark (approximately 60 mL) and kept under argon at atmospheric pressure. The cryoscopic vessel was placed in a conical glass jacket, which was evacuated to 10^{-1} mbar and cooled by dipping into liquid nitrogen. A cooling rate of initially 5 K/min resulted, which decreased to 1 K/min at the freezing point. Several independent measurements of the melting point of THF gave a value of 164.584 ± 0.0016 K. The cryoscopic constant E_K = 1.856 ± 0.016 K·kg/mol was determined by

Table 14. Crystal data and parameter of data collection for the sulfones *endo*-**5**, *exo*-**5** and *endo*-**6**

Compound	*endo*-**5**	*exo*-**5**	*endo*-**6**
(a) Crystal data			
Formula	$C_{14}H_{14}O_2S$	$C_{14}H_{14}O_2S$	$C_{14}H_{16}O_2S$
M_r	246.33	246.33	248.35
Color and habit	colorless, irregular	colorless, irregular	colorless, irregular
Crystal size [mm]	0.3 × 0.3 × 0.5	0.3 × 0.3 × 0.5	0.3 × 0.3 × 0.3
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_1/a$ (No. 14)
a, [Å]	9.5497(9)	8.0072(5)	12.185(3)
b, [Å]	11.2103(9)	11.393(1)	8.968 (1)
c, [Å]	11.5464(7)	13.622(1)	12.305(3)
α [°]	90	90	90
β [°]	90	90	111.497(9)
γ [°]	90	90	90
V [Å^3]	1236.1	1242.68	1251.07
Z	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.323	1.317	1.318
μ [cm^{-1}]	21.68	21.57	21.43
(b) Data collection			
diffractometer	CDA4 Enraf-Nonius	CDA4 Enraf-Nonius	CDA4 Enraf-Nonius
T [°C]	25	25	25
Radiation	Cu-K_α	Cu-K_α	Cu-K_α
λ [Å]	1.54179	1.54179	1.54179
Monochromator	graphite	graphite	graphite
Scan method	Ω/2Θ	Ω/2Θ	Ω/2Θ
Θ_{max} [°]	75.2	75.2	75.2
No. of data collected	3297	5785	5898
No. of unique data	1492	1506	2750
Observation criterion	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$
(c) Refinement			
No. of parameters refined	155	155	154
No. of data observed in refinement	1074	1288	2079
R, R_w[a]	0.056, 0.047	0.046, 0.040	0.054, 0.049
Extinction *r**	not refined	not refined	not refined
Δ(ρ) [e Å^{-3}]	−0.4/+0.3	−0.4/+0.3	−0.4/+0.3
GOF	2.522	2.401	2.058

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{0.5}$; $w = 1/\sigma^2(F_o)$ where F_o and F_c are observed and calculated structure factors.

Table 15. Crystal data and parameter of data collection for the lithiosulfones **3** and **4**

Compound	**3**	**4**
(a) Crystal data		
Formula	$(C_{20}H_{27}LiO_5S)_2$	$(C_{20}H_{29}LiO_5S)_2$
M_r	772.94	776.98
Color and habit	yellow, flat prism	yellow, flat prism
Crystal size [mm]	1.30 × 0.62 × 0.25	1.62 × 0.65 × 0.20
Crystal system	monoclinic	triclinic
Space group	*P*21/*c*	*P*−1 (No. 2)
a [Å]	9.161(9)	11.118(8)
b [Å]	21.240(3)	10.840(8)
c [Å]	12.690(2)	9.388(8)
α [°]	90.0	80.62(3)
β [°]	122.18(5)	76.45(3)
γ [°]	90.0	76.50(3)
V [Å^3]	2089.9(21)	1062.5(14)
Z	4	2
$D_{calcd.}$ [g cm^{-3}]	1.228	1.214
μ [cm^{-1}]	0.171	0.169
(b) Data collection		
Diffractometer	Stoe-STADI4	Stoe-STADI4
T [°C]	23	25
Radiation	Mo-K_α	Mo-K_α
λ [Å]	0.71069	0.71069
Monochromator	graphite	graphite
Scan method	Ω/2Θ	Ω
Θ_{max} [°]	20.03	20.09
No. of data collected	2606	2449
No. of unique data	1957	2007
Observation criterion	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$
No. of data observed	1571	1743
(c) Refinement		
No. of parameters refined	325	331
R, R_w[a]	0.0527, 0.1382	0.0383, 0.1067
Extinction r*	not refined	not refined
Δ(ρ) [e Å^{-3}]	−0.3/+0.2	−0.2/+0.2
GOF	1.061	1.031

[a] $R = (\Sigma||F_o| - |Fc||)/\Sigma|F_o|$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{0.5}$; $w = 1/\sigma^2(F_o)$ where F_o and F_c are observed and calculated structure factors.

measurement of solutions of naphthalene and *trans*-stilbene in THF (c = 0.044−0.045 mol/kg).

General: All reactions were carried out in absolute solvents under argon with syringe and Schlenk techniques in oven-dried glassware. Glass tubes containing solutions of lithiosulfones for NMR spectroscopy were sealed under argon. THF and ether were distilled under argon from potassium/benzophenone and sodium/benzophenone, respectively. Toluene was distilled from sodium and methanol was dried with magnesium and distilled. − ^{1}H, ^{13}C and ^{6}Li NMR: Varian VXR 300, Varian Gemini 300, Varian Unity 500, Bruker AC-300 spectrometers, chemical shifts reported relative to TMS (^{1}H, ^{13}C) and LiBr (^{6}Li), NMR chemical shifts of minor isomers obtained as mixture with major isomers given only when an unequivocal assignment was possible. − GC: Chrompack CP-9000 (DB-5: 30 m, 0.32 mm; 50 kPa H_2; *S1*: 100°C, 5 min, 20°C/min, 250°C, 5 min, 30°C/min, 300°C, 15 min; *S2*: 50°C, 5 min, 30°C/min, 150°C, 2 min, 20°C/min, 250°C, 2 min, 10°C/min, 300°C, 15 min) and Carlo Erba Mega Series 5300 [permethyl-β-cyclodextrin/polysiloxane (β-CD): 25 m, 0.25 mm; 100 kPa H_2; 100°C, 2 min, 150°C, 5 min, 170°C, 5 min, 200°C, 30 min] instruments. − GC MS: Magnum Finnigan (HT-5: 25 m, 0.25 mm; 50 kPa He, CI, 40 eV, MeOH). − MS: Varian MAT 212S (EI, 70 eV), decisive signals of the MS spectra and those with an intensity higher than 10% are listed. − Column chromatography: Merck silica gel 60, 0.063−0.200 mm. − TLC: Merck silica gel 60 F_{254} plates. − Elementary analyses: Microanalytical laboratories of the Institut für Organische Chemie at the RWTH Aachen and the Institut für Organische Chemie und Biochemie at the University of Freiburg.

(±)-*endo*- and (±)-*exo*-3-Methylene-2-(phenylsulfonyl)bicyclo[2.2.1]-hept-5-ene (*endo*-5 and *exo*-5): 1,2-Phenyl propadienyl sulfone (12.6 g, 0.07 mol) and cyclopentadiene (13.2 g, 0.20 mol) in toluene (150 mL) were heated to reflux for 2 h. Evaporation of the solvent gave a mixture of *endo*-**5** and *exo*-**5** in a ratio of 2:1 as an orange oil. Chromatography (EtOAc/*n*-hexane, 1:2) and crystallization from EtOAc/*n*-hexane (1:5) afforded *endo*-**5** (7.6 g, 44%) and *exo*-**5** (3.6 g, 21%) as colorless crystals.

***endo*-5**: M.p. 64°C. − MS; *m*/*z* (%): 246 [M$^+$] (12), 121 (39), 106 (10), 105 (100), 103 (18), 79 (28), 78 (11), 77 (42), 66 (14), 51 (16), 44 (11), 40 (23), 39 (14). − $C_{14}H_{14}O_2S$ (246.3): calcd. C 68.27, H 5.73; found C 68.49, H 5.80.

***exo*-5:** M.p. 53°C. − MS; *m*/*z* (%): 246 [M$^+$] (3), 121 (39), 106 (11), 105 (100), 103 (13), 79 (36), 77 (37), 65 (6), 51 (9), 39 (5). − $C_{14}H_{14}O_2S$ (246.3): calcd. C 68.27, H 5.73; found C 68.00, H 5.66.

(±)-*endo*-3-Methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (*endo*-6): A mixture of Pd/C (10%) (1 g) and *endo*-**5** (0.500 g, 2.0 mmol) in MeOH (70 mL) was vigorously stirred under H_2 at room temp. After 17 min, the theoretical amount of H_2 had been taken up and hydrogenation was terminated by removal of the catalyst by filtration through Celite. Concentration of the solution in vacuo gave *endo*-**6** (360 mg, 72%) as colorless crystals. − M.p. 100°C (EtOAc/*n*-hexane, 1:3). − MS; *m*/*z* (%): 248 [M$^+$] (2), 220 (5), 108 (10), 107 (87), 105 (11), 91 (41), 80 (13), 79 (100), 78 (22), 77 (78), 65 (16), 53 (15), 51 (9). − $C_{14}H_{16}O_2S$ (248.3): calcd. C 67.71, H 6.49; found C 67.33, H 6.50.

(±)-*exo*-3-Methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (*exo*-6): A mixture of Pd/C (10%) (1 g) and *exo*-**5** (0.500 g, 2.0 mmol) in MeOH (70 mL) was vigorously stirred under H_2 at room temp. After 15 min, the theoretical amount of H_2 had been taken up and hydrogenation was terminated by removal of the catalyst by filtration through Celite. Concentration of the solution in vacuo gave *exo*-**6** (420 mg, 84%) as colorless crystals. − M.p. 71°C (EtOAc/*n*-hexane, 1:3). − MS; *m*/*z* (%): 248 [M$^+$] (4), 220 (3), 109 (12), 108 (8), 107 (100), 91 (12), 79 (57), 78 (6), 77 (16), 65 (3), 51 (5). − $C_{14}H_{16}O_2S$ (248.3): calcd. C 67.71, H 6.49; found C 67.49, H 6.54.

Lithium·2digylme (±)-3-Methylene-2-(phenylsulfonyl)bicyclo[2.2.1]-hept-5-ene-2-ide (*endo*-3/ent-*endo*-3·2diglyme): A solution of *exo*-**5** (100 mg, 0.40 mmol) in ether (2 mL) was added at −78°C to a solution of *n*PrLi (0.5 mL, 0.84 M in *n*-hexane, 0.40 mmol) in ether (2 mL), whereby the solution turned orange. After addition of diglyme (4 mL, 28 mmol) to the solution, it was warmed to room temp. and concentrated in vacuo until most of *n*-hexane and ether had been removed. The resulting suspension was warmed to 50°C, until all of the solid was dissolved. The solution was allowed to cool slowly to room temp. and kept for 2 d at this temp. The solid was removed by filtration, washed with *n*-hexane and dried in vacuo to give *endo*-**3**/ent-*endo*-**3**·2diglyme (110 mg, 71%) as yellow crystals. − ^{6}Li NMR (44.17 MHz, [D$_8$]THF): δ = −0.74 (s).

Lithium·2diglyme (±)-3-Methylene-2-(phenylsulfonyl)bicyclo[2.2.1]-heptane-2-ide (*endo*-4/ent-*endo*-4·2diglyme): A solution of *exo*-**6** (100 mg, 0.40 mmol) in ether (2 mL) was added at −78°C to a solution of *n*PrLi (0.5 mL, 0.84 M in *n*-hexane, 0.40 mmol) in ether (2 mL) whereby the solution turned red. After addition of diglyme (4 mL, 28 mmol) to the solution, it was warmed to room temp. and concentrated in vacuo until most of *n*-hexane and ether had been removed. The resulting suspension was warmed to 50°C, until all

of the solid was dissolved. The solution was allowed to cool slowly to room temp. and kept at this temp. for 2 d. The solid was removed by filtration, washed with *n*-hexane and dried in vacuo to give *endo*-**4**/ent-*endo*-**4**·2diglyme (134 mg, 81%) as yellow crystals. – ^{6}Li NMR (44.17 MHz, [D$_8$]THF): δ = −0.76 (s).

Determination of Aggregation of Lithiosulfones 3 and 4: The sulfone (2.70 mmol) was placed in an argon-filled weighed Schlenk flask and THF (10 mL) was added followed by the dropwise addition of *n*BuLi (1.69 mL, 1.6 M in *n*-hexane) at −78°C. After warming the solution to room temp., the volatiles were removed in vacuo and the residue dried for 10 min at 10^{-3} mbar. The amount of lithiosulfones was determined by differential weighing. The amount of coordinated THF was determined by ^{1}H-NMR spectroscopy in an independent experiment. The lithiosulfone was dissolved by addition of THF (63 mL) and the flask was weighed again. Thus, solutions with c_{nom} = 0.0497−0.0503 mol/kg were obtained. In each cryoscopic experiment the solution was frozen and thawed and the cooling curves were measured at least seven times, whereby attention was paid that at the cooling branch no precipitation of the lithiosulfone occurred. After the registration of the cooling curves, the solution was warmed to −80°C and treated with CF_3COOD (5 mL, 10 mmol). The solution was washed with satd. aqueous $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated in vacuo to give the starting sulfone, whose degree of deuteration (C2) was determined by ^{1}H-NMR spectroscopy. The melting point depression ΔT of each solution was determined by linear regressions of the successive cooling curves and by averaging the results. The equation $n = c_{nom}\cdot E_K/\Delta T$ was used for determination of the degree of aggregation (Table 16).

The D content of the recovered sulfone was only in the range of 94.5−98%. Several factors including the use of an insufficient amount of *n*BuLi, an incomplete deuteration and a hydrolysis of the lithiosulfone during preparation and/or measurement could be responsible for the partial recovery of the H-sulfone. We think that the major factor is hydrolysis of the lithiosulfone. We have thus corrected the aggregation number under the assumption that formation of the H-sulfone is solely caused by hydrolysis of the lithiosulfone under formation of H-sulfone and LiOH and that both are monomeric in THF.

General Procedure for Reaction of Lithiosulfones 3 and 4 with Electrophiles: *n*BuLi (0.14 mL, 1.6 M in *n*-hexane, 0.22 mmol) was added dropwise at −78°C to a solution of *endo*-**5** or *exo*-**5** and *endo*-**6** or *exo*-**6** (50 mg, 0.2 mmol) in THF (5 mL). After addition of the first drop of the base, the solution turned immediately yellow and yellow/orange, respectively. Stirring was continued for 40 min to give deep yellow and yellow/orange solutions of **3** and **4**, respectively. The electrophile was added to the solution of **3** and **4** at −78°C, whereby decolorization occurred except otherwise stated. After stirring the solution for 10−15 min at this temp., it was warmed to room temp. during 1.5 h. Subsequently, satd. aqueous $NaHCO_3$ (20 mL) was added and the mixture was extracted with ether (20 mL). The combined organic phases were washed with satd. aqueous $NaHCO_3$ (40 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane, 1:2) afforded a mixture of the corresponding *endo* and *exo* sulfones as colorless solids or oils.

(±)-*endo*- and (±)-*exo*-2-Deuterio-3-methylene-2-(phenylsulfonyl)-bicyclo[2.2.1]hept-5-ene (*endo*-8a and *exo*-8a): CF_3COOD (0.09 mL, 1.2 mmol) or DCl/D_2O (0.2 mL, 10 M, 2 mmol) were added to the solution of **3**, which became immediately colorless. Workup gave a mixture of *endo*-**8a** and *exo*-**8a** (47 mg, 95%) in a ratio of 87:13 (GC) or a mixture of *endo*-**8a** and *exo*-**8a** (45 mg, 91%) in a ratio of 88:12 (GC) as colorless oils.

***endo*-8a:** GC: t_R = 13.01 min (DB-5, *S2*). – ^{1}H NMR(300 MHz, $CDCl_3$): δ = 1.45 (dm, $J_{7s,7a}$ = 8.7 Hz, 1 H, H-7$_s$), 1.64 (dm, $J_{7a,7s}$ = 8.7 Hz, 1 H, H-7$_a$), 3.03 (s, 1 H, H-1), 3.30 (s, 1 H, H-4), 5.26 (s, 1 H, H-8$_a$), 5.33 (s, 1 H, H-8$_s$), 6.06 (dd, $J_{6,5}$ = 5.7, $J_{6,1}$ = 2.6 Hz, 1 H, H-6), 6.14 (dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 3.3 Hz, 1 H, H-5), 7.55 (tm, 2 H, H-11,13), 7.65 (tm, 1 H, H-12), 7.89 (dm, 2 H, H-10,14). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.34 (C-1), 49.77 (C-7), 52.26 (C-4), 110.01 (C-8), 128.67 (C-10,14), 128.99 (C-11,13), 133.06 (C-6), 133.59 (C-12), 135.09 (C-5), 139.43 (C-9), 143.11 (C-3). – GC MS; *m*/*z* (%): 248 [M$^+$ + 1] (5), 184 (8), 122 (3), 106 (8), 89 (100), 61 (46).

***exo*-8a:** GC: t_R = 12.90 min (DB-5, *S2*). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7$_a$), 2.03 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7$_s$), 3.17 (s, 1 H, H-1), 3.29 (s, 1 H, H-4), 5.13 (d, 1 H, H-8$_s$), 5.29 (s, 1 H, H-8$_a$), 6.11 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 3.0 Hz, 1 H, H-6), 6.28 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 3.0 Hz, 1 H, H-5), 7.58 (tm, 2 H, H-11,13), 7.67 (tm, 1 H, H-12), 7.93 (dm, 2 H, H-10,14). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.65 (C-1), 46.29 (C-7), 50.67 (C-4), 111.15 (C-8), 128.88 (C-10,14), 129.16 (C-11,13), 133.68 (C-12), 135.55 (C-6), 139.04 (C-9), 139.94 (C-5), 142.83 (C-3). – GC MS; *m*/*z* (%): 248 [M$^+$ + 1] (16), 122 (15), 106 (15), 89 (100), 61(44).

***endo*-8a/*exo*-8a:** $C_{14}DH_{13}O_2S$ (247.3): calcd. C 67.99, H 5.30; found C 68.14, H 5.41.

(±)-*endo*- and (±)-*exo*-2-Deuterio-3-methylene-2-(phenylsulfonyl)-bicyclo[2.2.1]-heptane (*endo*-9a and *exo*-9a): CF_3COOD (0.09 mL, 1.2 mmol) was added to the solution of **4**, which became immediately colorless. Workup gave a mixture of *endo*-**9a** and *exo*-**9a** (44 mg, 88%) in a ratio of 59:41 (GC) as a colorless oil.

***endo*-9a:** GC: t_R = 23.48 min (β-CD). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (sm, 2 H, H-7$_s$, H-7$_a$), 1.40 (m, 1 H, H-6), 1.58 (m, 1 H, H-5), 1.73 (m, 1 H, H-5), 2.37 (m, 2 H, H-1,H-6), 2.84 (s, 1 H, H-4), 5.14 (s, 1 H, H-8$_a$), 5.17 (s, 1 H, H-8$_s$), 7.57 (tm, 2 H, H-11,13), 7.65 (tm, 1 H, H-12), 7.94 (dm, 2 H, H-10,14). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.90 (C-6), 28.18 (C-5), 39.17 (C-7), 40.55 (C-1), 47.06 (C-4), 108.57 (C-8), 128.30 (C-10,14), 129.27 (C-11,13), 133.55 (C-12), 140.35 (C-9), 146.04 (C-3). – GC MS;

Table 16. Cryoscopy of lithiosulfones **3** and **4** in THF

Lithiosulfone	c_{nom} [mol/kg]	ΔT [K]	c_{exp} [mol/kg]	*n*	D content of sulfone [%]	n_{cor}[a]
3	0.0497	0.058	0.0313		94.5	
3	0.0498	0.071	0.0383		97	
3	0.0503	0.064	0.0345	1.45±0.08[b]	97	1.58±0.13[b]
4	0.0500	0.062	0.0334		98	
4	0.0503	0.058	0.0313	1.56±0.06[b]	98	1.62±0.06[b]

[a] $n_{cor} = c_{nom} - c_{H\text{-}sulfone}/c_{exp} - 2\ c_{H\text{-}sulfone}$. – [b] Mean value.

m/*z* (%): 250 [M^+ + 1] (77), 215 (31), 184 (2), 124 (5), 108 (100), 80 (8), 61(2).

***exo*-9a:** GC: t_R = 22.66 min (β-CD). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (dm, 1 H, H-7_s), 1.23 (m, 1 H, H-6), 1.33 (tm, 1 H, H-5), 1.66 (dm, 2 H, H-5, H-6), 1.86 (dm, 1 H, H-7_a), 2.64 (s, 1 H, H-1), 2.79 (s, 1 H, H-4), 5.14 (s, 1 H, H-8_s), 5.19 (s, 1 H, H-8_a), 7.56 (tm, 2 H, H-11,13), 7.66 (tm, 1 H, H-12), 7.91 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.43 (C-6), 29.84 (C-5), 36.05 (C-7), 40.27 (C-1), 45.32 (C-4), 110.19 (C-8), 129.07 (C-10,14), 129.15 (C-11,13), 133.68 (C-12), 139.00 (C-9), 146.81 (C-3). − GC MS; *m*/*z* (%): 250 [M^+ + 1] (84), 215 (25), 184 (2), 171 (3), 124 (3), 108 (100), 80 (13), 61(7).

***endo*-9a/*exo*-9a:** $C_{14}DH_{15}O_2S$ (249.3): calcd. C 67.44, H 6.06; found C 67.20, H 6.03.

(±)-*endo*- and (±)-*exo*-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-8b and *exo*-8b): Neat MeI (0.14 mL, 2.2 mmol) was added to the solution of **3**, which turned immediately pale yellow. Workup gave a mixture of *endo*-**8b** and *exo*-**8b** (44 mg, 85%) in a ratio of 77:23 (GC) as a colorless solid.

***endo*-8b:** GC: t_R = 23.63 min (β-CD). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7_a), 1.73 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7_s), 1.73 (s, 3 H, Me), 2.83 (s, 1 H, H-1), 3.28 (s, 1 H, H-4), 5.29 (s, 1 H, H-8_a), 5.42 (s, 1 H, H-8_s), 5.98 (dd, $J_{6,5}$ = 5.7 Hz, $J_{6,1}$ = 3.0 Hz, 1 H, H-6), 6.21 (dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 3.0 Hz, 1 H, H-5), 7.50 (tm, 2 H, H-11,13), 7.58 (tm, 1 H, H-12), 7.87 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.67 (Me), 49.33 (C-7), 51.55 (C-1), 52.42 (C-4), 73.01 (C-2), 109.97 (C-8), 128.49 (C-11,13), 130.14 (C-10,14), 133.38 (C-5), 134.94 (C-12), 136.40 (C-6), 138.97 (C-9), 149.46 (C-3). − GC MS; *m*/*z* (%): 261 (91) [M^+ + 1], 237 (5), 209 (3), 197 (13), 181 (3), 135 (6), 119 (100), 91 (6).

***exo*-8b:** GC: t_R = 24.07 min (β-CD). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 3 H, Me), 1.55 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7_a), 2.57 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7_s), 3.10 (s, 1 H, H-1), 3.34 (s, 1 H, H-4), 5.19 (s, 1 H, H-8_s), 5.32 (s, 1 H, H-8_a), 6.09 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 3.0 Hz, 1 H, H-6), 6.31 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 3.0 Hz, 1 H, H-5), 7.56 (tm, 2 H, H-11,13), 7.66 (tm, 1 H, H-12), 7.93 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.23 (Me), 48.01 (C-7), 50.41 (C-1), 51.81 (C-4), 72.46 (C-2), 110.86 (C-8), 128.81 (C-11,13), 130.47 (C-10,14), 133.62 (C-12), 135.90 (C-5), 137.97 (C-9), 139.83 (C-6), 148.76 (C-3). − GC MS; *m*/*z* (%): 261 [M^+ + 1] (34), 233 (2), 197 (4), 183 (3), 135 (3), 119 (100), 91 (11), 89 (14), 61 (9).

***endo*-8b/*exo*-8b:** $C_{15}H_{16}O_2S$ (260.4): calcd. C 69.20, H 6.19; found C 69.13, H 6.21.

(±)-*endo*- and (±)-*exo*-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (*endo*-9b and *exo*-9b): Neat MeI (0.14 mL, 2.2 mmol) was added to the solution of **4**, which immediately turned pale yellow. Workup gave a mixture of *endo*-**9b** and *exo*-**9b** (47 mg, 90%) in a ratio of 81:19 (GC) as a colorless solid.

***endo*-9b:** GC: t_R = 13.47 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36 (dm, $J_{7a,7s}$ = 10.0 Hz, 1 H, H-7_a), 1.44 (s, 3 H, Me), 1.49 (m, 1 H, H-6), 1.63 (dm, $J_{7s,7a}$ = 10.0 Hz, 1 H, H-7_s), 1.70 (m, 2 H, H-5), 2.23 (m, 1 H, H-1), 2.65 (m, 1 H, H-6), 2.85 (s, 1 H, H-4), 5.12 (s, 1 H, H-$8_{a,s}$), 5.13 (s, 1 H, H-$8_{a,s}$), 7.55 (tm, 2 H, H-11,13), 7.64 (tm, 1 H, H-12), 7.96 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.41 (Me), 25.58 (C-6), 26.74 (C-5), 38.46 (C-7), 47.05 (C-1), 47.26 (C-4), 72.73 (C-2), 107.79 (C-8), 128.47 (C-11,13), 130.15 (C-10,14), 133.43 (C-12), 138.60 (C-9), 153.04 (C-3). − GC MS; *m*/*z* (%): 263 [M^+ + 1] (7), 241 (7), 121 (100), 93 (10), 89 (5), 79 (4), 61 (4).

***exo*-9b:** GC: t_R = 13.54 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (dm, $J_{7a,7s}$ = 10.0 Hz, 1 H, H-7_a), 1.29 (m, 1 H, H-5), 1.52 (s, 3 H, Me), 1.53 (m, 2 H, H-6), 1.72 (m, 1 H, H-5), 2.32 (dm, $J_{7s,7a}$ = 10.0 Hz, 1 H, H-7_s), 2.55 (s, 1 H, H-1), 2.80 (s, 1 H, H-4), 5.17 (s, 2 H, H-8_a, H-8_s), 7.55 (tm, 2 H, H-11,13), 7.64 (tm, 1 H, H-12), 7.91 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.54 (Me), 24.98 (C-6), 29.42 (C-5), 37.50 (C-7), 44.76 (C-1), 46.23 (C-4), 72.03 (C-2), 108.57 (C-8), 128.76 (C-11,13), 130.53 (C-10,14), 133.54 (C-12), 137.67 (C-9), 153.53 (C-3). − GC MS; *m*/*z* (%): 263 [M^+ + 1] (9), 241 (8), 121 (100), 93 (14), 89 (33), 79 (10), 61 (21).

***endo*-9b/*exo*-9b:** $C_{15}H_{18}O_2S$ (262.4): calcd. C 68.67, H 6.91; found C 68.67, H 6.91.

(±)-*endo*- and (±)-*exo*-2-Ethyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-8c and *exo*-8c): Neat EtI (0.17 mL, 2.0 mmol) was added to the solution of **3**, which became light yellow. The solution was stirred for 30 min at −78°C and warmed within 15 min to −45°C whereby it turned colorless. Workup gave a mixture of *endo*-**8c** and *exo*-**8c** (46 mg, 84%) in a ratio of 83:17 (GC) as a colorless solid.

***endo*-8c:** GC: t_R = 11.32 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.39 Hz; 3 H, Me), 1.59 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7_a), 1.69 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7_s), 1.95 (m, 1 H, CH_2), 2.57 (m, 1 H, CH_2), 3.21 (s, 1 H, H-4), 3.28 (s, 1 H, H-1), 5.25 (s, 1 H, H-8_a), 5.36 (s, 1 H, H-8_s), 5.67 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 3.0 Hz, 1 H, H-5), 6.12 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 3.3 Hz, 1 H, H-6), 7.42 (tm, 2 H, H-11,13), 7.54 (tm, 1 H, H-12), 7.83 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.24 (Me), 30.57 (CH_2), 48.22 (C-1), 48.67 (C-7), 52.07 (C-4), 77.85 (C-2), 110.35 (C-8), 127.91 (C-11,13), 130.31 (C-10,14), 132.97 (C-12), 135.67 (C-5), 136.80 (C-6), 140.70 (C-9), 149.59 (C-3). − GC MS; *m*/*z* (%): 275 [M^+ + 1] (1), 237 (1), 133 (100), 105 (4), 89 (4), 61 (2).

***exo*-8c:** GC: t_R = 11.33 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 7.39 Hz; 3 H, Me), 1.40 (m, 1 H, CH_2), 1.51 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7_a), 2.06 (m, 1 H, CH_2), 2.26 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7_s), 3.26 (s, 1 H, H-4), 3.55 (s, 1 H, H-1), 4.95 (s, 1 H, H-8_s), 5.22 (s, 1 H, H-8_a), 6.22 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 2.6 Hz, 1 H, H-6), 6.27 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 3.0 Hz, 1 H, H-5), 7.50 (tm, 2 H, H-11,13), 7.63 (tm, 1 H, H-12), 7.92 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.51 (Me), 31.04 (CH_2), 47.19 (C-7), 48.67 (C-1), 51.56 (C-4), 110.23 (C-8), 128.58 (C-11,13), 130.45 (C-10,14), 133.43 (C-12), 135.36 (C-5), 139.22 (C-9), 139.98 (C-6), 150.08 (C-3). − GC MS; *m*/*z* (%): 275 [M^+ + 1] (5), 133 (2), 89 (100), 61 (44).

***endo*-8c/*exo*-8c:** $C_{16}H_{18}O_2S$ (274.4): calcd. C 70.04, H 6.61; found C 69.99, H 6.64.

(±)-*endo*- and (±)-*exo*-2-Ethyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (*endo*-9c and *exo*-9c): Neat EtI (0.17 mL, 2.0 mmol) was added to the solution of **4** which turned yellow. The solution was stirred for 30 min at −78°C and warmed within 15 min to −45°C whereby it became pale yellow. Workup gave a mixture of *endo*-**9c** and *exo*-**9c** (50 mg, 91%) in a ratio of 95:5 (GC) as a colorless solid.

***endo*-9c:** GC: t_R = 11.61 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.39 Hz; 3 H, Me), 1.33 (dm, $J_{7s,7a}$ = 10.0 Hz, 1 H, H-7_s), 1.50−1.90 (m, 6 H, H-5, H-5, H-6, H-7_a, CH_2), 1.60 (dm, $J_{7a,7s}$ = 10.0 Hz, 1 H, H-7_a), 1.75 (m, 1 H, CH_2), 1.84 (m, 1 H, CH_2), 2.58 (m, 1 H, H-6), 2.65 (s, 1 H, H-4), 2.82 (s, 1 H, H-1), 4.97 (s, 1 H, H-$8_{a,s}$), 5.13 (s, 1 H, H-$8_{a,s}$), 7.52 (tm, 2 H, H-11,13), 7.63 (tm, 1 H, H-12), 7.97 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.81 (Me), 25.58 (CH_2), 27.28 (C-6),

30.37 (C-5), 37.96 (C-7), 44.23 (C-1), 47.24 (C-4), 76.88 (C-2), 108.06 (C-8), 128.64 (C-11,13), 130.24 (C-10,14), 133.37 (C-12), 139.84 (C-9), 153.03 (C-3). − GC MS; *m*/*z* (%): 277 [M^+ + 1] (33), 135 (12), 125 (3), 89 (100), 61 (53).

***exo*-9c:** GC: t_R = 11.88 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 7.05 Hz; 3 H, Me) 4.93 (s, 1 H, H-$8_{a,s}$), 5.11 (s, 1 H, H-$8_{a,s}$), 7.87 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.90 (C-11,13), 129.49 (C-10,14). − GC MS; *m*/*z* (%): 277 [M^+ + 1] (1), 137 (1), 125 (2), 89 (100), 61 (53).

***endo*-9c/*exo*-9c:** $C_{16}H_{20}O_2S$ (276.4): calcd. C 69.53, H 7.29; found C 69.41, H 7.29.

(±)-*endo*- and (±)-*exo*-3-Methylene-2-(phenylsulfonyl)-2-propylbicyclo[2.2.1]hept-5-ene (*endo*-8d and *exo*-8d): Neat *n*PrI (0.2 mL, 2.0 mmol) was added to the solution of **3**, which became light yellow. The solution was warmed within 35 min to −60 °C whereby it became colorless. Workup gave a mixture of *endo*-**8d** and *exo*-**8d** (50 mg, 87%) in a ratio of 89:11 (GC) as a colorless solid.

***endo*-8d:** GC: t_R = 9.50 min (DB−5, 150 °C, isotherm, 100 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3 H, Me), 1.59 (dm, $J_{7s,7a}$ = 8.7 Hz, 1 H, H-7_s), 1.71 (dm, $J_{7a,7s}$ = 8.7 Hz, 1 H, H-7_a), 1.75 (m, 2 H, $CH_3-CH_2-CH_2$), 1.84 (dt, *J* = 12.7, *J* = 4.7 Hz, 1 H, CH_2), 2.44 (dt, 1 H, *J* = 12.7, *J* = 4.7 Hz, CH_2), 3.19 (s, 1 H, H-4), 3.27 (s, 1 H, H-1), 5.25 (s, 1 H, H-$8_{a,s}$), 5.35 (s, 1 H, H-$8_{a,s}$), 5.67 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 3.3 Hz, 1 H, H-5), 6.12 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 3.0 Hz, 1 H, H-6), 7.42 (tm, 2 H, H-11,13), 7.55 (tm, 1 H, H-12), 7.82 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.73 (Me), 18.77 (CH_2), 39.96 (CH_2), 48.78 (C-1, C-7), 52.18 (C-4), 77.91 (C-2), 110.32 (C-8), 128.02 (C-11,13), 130.38 (C-10,14), 133.08 (C-12), 135.71 (C-5), 136.94 (C-6), 140.76 (C-9), 149.89 (C-3). − GC MS; *m*/*z* (%): 289 [M^+ + 1] (2), 147 (100), 119 (1), 89 (1), 69 (1).

***exo*-8d:** GC: t_R = 9.43 min (DB−5, 150 °C, isotherm, 100 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, *J* = 7.3 Hz; 3 H, Me), 1.50 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7_a), 1.70 (m, 2 H, Me−CH_2), 1.84 (m, 1 H, CH_2), 2.23 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7_s), 2.44 (m, 1 H, CH_2), 3.27 (s, 1 H, H-4), 3.55 (s, 1 H, H-1), 4.97 (s, 1 H, H-8_s), 5.22 (s, 1 H, H-8_a), 6.20 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 3.0 Hz, 1 H, H-6), 6.27 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 3.3 Hz, 1 H, H-5), 7.51 (tm, 2 H, H-11,13), 7.63 (tm, 1 H, H-12), 7.91 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.72 (Me), 19.09 (CH_2), 40.49 (CH_2), 47.35 (C-7), 48.65 (C-1), 51.56 (C-4), 76.73 (C-2), 110.24 (C-8), 128.69 (C-11,13), 130.49 (C-10,14), 133.55 (C-12), 135.49 (C-5), 140.10 (C-6). − GC MS; *m*/*z* (%): 289 [M^+ + 1] (1), 147 (100), 119 (4), 105 (8), 89 (26), 69 (4), 61 (12).

***endo*-8d/*exo*-8d:** $C_{17}H_{20}O_2S$ (288.4): calcd. C 70.80, H 6.99; found C 70.63, H 6.99.

(±)-*endo*- and (±)-*exo*-3-Methylene-2-(phenylsulfonyl)-2-propylbicyclo[2.2.1]heptane (*endo*-9d and *exo*-9d): Neat *n*PrI (0.2 mL, 2.0 mmol) was added to the solution of **4**, whose color did not change. The solution was warmed slowly to −40 °C whereby it became colorless. Workup gave a mixture of *endo*-**9d** and *exo*-**9d** (55 mg, 95%) in a ratio of 97:3 (GC) as a colorless solid.

***endo*-9d:** GC: t_R = 11.93 min (DB-5, *S1*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 7.0 Hz; 3 H, Me), 1.30−1.80 (m, 9 H, H-5, H-5, H-6, H-7, H-7, CH_2), 1.34 (dm, $J_{7s,7a}$ = 10.0 Hz, 1 H, H-7_s), 1.67 (dm, $J_{7a,7s}$ = 10.0 Hz, 1 H, H-7_a), 2.59 (m, 1 H, H-6), 2.65 (s, 1 H, H-4), 2.81 (s, 1 H, H-1), 4.96 (s, 1 H, H-$8_{a,s}$), 5.11 (s, 1 H, H-$8_{a,s}$), 7.52 (tm, 2 H, H-11,13), 7.63 (tm, 1 H, H-12), 7.96 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.43 (Me), 18.13 (CH_2), 25.54 (C-6), 27.20 (C-5), 37.86 (C-7), 39.75 (CH_2), 44.53 (C-1), 47.23 (C-4), 76.93 (C-2), 107.75 (C-8), 128.56 (C-11,13), 130.10 (C-10,14), 133.32 (C-12), 139.79 (C-9), 153.36 (C-3). − GC MS; *m*/*z* (%): 291 [M^+ + 1] (40), 149 (7), 125 (3), 89 (100), 61 (46).

***exo*-9d:** GC: t_R = 11.85 min (DB-5, *S1*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.98 (s, 1 H, H-$8_{a,s}$), 5.13 (s, 1 H, H-$8_{a,s}$). − GC MS; *m*/*z* (%): 291 [M^+ + 1] (1), 149 (100), 121 (2), 107 (4), 89 (17), 79 (4), 61 (10).

***endo*-9d/*exo*-9d:** $C_{17}H_{22}O_2S$ (290.4): calcd. C 70.31, H 7.63; found C 70.03, H 7.69.

(±)-*endo*- and (±)-*exo*-2-Hexyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-8e and *exo*-8e): Neat *n*HeI (0.3 mL, 2.0 mmol) was added to the solution of **3**, whose color did not change. The solution was warmed within 35 min to −60 °C whereby it became colorless. Workup gave a mixture of *endo*-**8e** and *exo*-**8e** (53 mg, 80%) in a ratio of 88:12 (GC) as a colorless oil.

***endo*-8e:** GC: t_R = 9.51 min (DB−5, 150 °C, isotherm, 100 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 3 H, Me), 1.2−1.8 (m, 10 H, H-7, H-7, CH_2), 1.59 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7_s), 1.71 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7_a), 1.85 (m, 1 H, CH_2), 2.47 (m, 1 H, CH_2), 3.19 (s, 1 H, H-4), 3.27 (s, 1 H, H-1), 5.25 (s, 1 H, H-$8_{a,s}$), 5.35 (s, 1 H, H-$8_{a,s}$), 5.68 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 3.3 Hz, 1 H, H-5), 6.13 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 3.0 Hz, 1 H, H-6), 7.42 (tm, 2 H, H-11,13), 7.54 (tm, 1 H, H-12), 7.84 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.05 (Me), 22.61 (CH_2), 25.19 (CH_2), 29.87 (CH_2), 31.52 (CH_2), 37.73 (CH_2), 48.65 (C-1, C-7), 52.06 (C-4), 77.71 (C-2), 110.18 (C-8), 127.91 (C-11,13), 130.27 (C-10,14), 132.95 (C-12), 135.62 (C-5), 136.82 (C-6), 140.66 (C-9), 149.85 (C-3). − GC MS; *m*/*z* (%): 331 [M^+ + 1] (2), 205 (1), 189 (100), 147 (2), 133 (4), 119 (4), 105 (3), 89 (17), 61 (10).

***exo*-8e:** GC: t_R = 9.43 min (DB−5, 150 °C, isotherm, 100 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 3 H, Me), 1.2−1.8 (m, 1 H, CH_2, H-7_a), 2.26 (dm, $J_{7s,7a}$ = 9.7 Hz, 1 H, H-7_s), 3.27 (s, 1 H, H-4), 3.54 (s, 1 H, H-1), 4.97 (s, 1 H, H-8_s), 5.22 (s, 1 H, H-8_a), 6.19 (dd, $J_{6,5}$ = 5.3, $J_{6,1}$ = 3.0 Hz, 1 H, H-6), 6.27 (dd, $J_{5,6}$ = 5.3, $J_{5,4}$ = 2.3 Hz, 1 H, H-5), 7.42 (tm, 2 H, H-11,13), 7.55 (tm, 1 H, H-12), 7.91 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.00 (Me), 22.60 (CH_2), 25.50 (CH_2), 29.77 (CH_2), 31.43 (CH_2), 38.28 (CH_2), 47.22 (C-7), 48.51 (C-1), 51.46 (C-4), 110.18 (C-8), 128.55 (C-11,13), 130.40 (C-10,14), 133.43 (C-12), 135.36 (C-5), 139.97 (C-6). − GC MS; *m*/*z* (%): 331 [M^+ + 1] (1), 205 (1), 189 (100), 147 (2), 133 (5), 119 (6), 105 (4), 89 (9), 61 (5).

***endo*-8e/*exo*-8e:** $C_{20}H_{26}O_2S$ (330.5): calcd. C 72.69, H 7.93; found C 72.69, H 8.00.

(±)-*endo*- and (±)-*exo*-2-Hexyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (*endo*-9e and *exo*-9e): Neat *n*HeI (0.3 mL, 2.0 mmol) was added to the solution of **4** whose color did not change. The solution was warmed slowly to −40 °C whereby it became colorless. Workup gave a mixture of *endo*-**9e** and *exo*-**9e** (54 mg, 81%) in a ratio of 97:3 (GC) as a colorless oil.

***endo*-9e:** GC: t_R = 8.97 min (DB−5, 150 °C, isotherm, 100 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 3 H, *J* = 7.05 Hz, Me), 1.00−1.90 (m, 15 H, CH_2, H-7, H-7, H-6, H-5, H-5), 1.34 (dm, $J_{7s,7a}$ = 10.0 Hz, 1 H, H-7_s), 1.67 (dm, $J_{7a,7s}$ = 10.0 Hz, 1 H, H-7_a), 2.59 (m, 1 H, H-6), 2.65 (s, 1 H, H-4), 2.81 (s, 1 H, H-1), 4.97 (s, 1 H, H-$8_{a,s}$), 5.11 (s, 1 H, H-$8_{a,s}$), 7.53 (tm, 2 H, H-11,13), 7.63 (tm, 1 H, H-12), 7.96 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.04 (Me), 22.57 (CH_2), 24.69 (CH_2), 25.52 (C-6), 27.21 (C-5), 29.73 (CH_2), 31.52 (CH_2), 37.63 (C-7), 37.86 (CH_2), 44.51 (C-1), 47.23 (C-4), 76.84 (C-2), 107.77 (C-8), 128.55 (C-11,13), 130.10 (C-10,14), 133.32 (C-12), 139.80 (C-9), 153.37 (C-

3). − GC MS; *m*/*z* (%): 333 [M^+ + 1] (19), 191 (100), 149 (6), 135 (18), 121 (14), 109 (8), 95 (11), 89 (73), 81 (8), 61 (43).

***exo*-9e:** GC: t_R = 8.88 min (DB−5, 150°C, isotherm, 100 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (m, 3 H, CH_3), 4.96 (s, 1 H, H-$8_{a,s}$). − GC MS; *m*/*z* (%): 191 [M^+ − SO_2Ph] (100), 149 (7), 135 (24), 121 (15), 109 (11), 95 (12), 89 (69), 81 (8), 69 (4), 61 (40).

***endo*-9e/*exo*-9e:** $C_{20}H_{28}O_2S$ (332.5): calcd. C 72.25, H 8.49; found C 71.92, H 8.32.

(±)-(1R*,9R*)-*endo*-2-[(1-Hydroxy-1-phenyl)methyl]-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene and (±)-*exo*-2-[(1-Hydroxy-1-phenyl)methyl]-3-methylene-2-(phenylsulfonyl)bicyclo-[2.2.1]hept-5-ene (*endo*-8f and *exo*-8f): Freshly distilled PhCHO (0.2 mL, 2.0 mmol) was added to the solution of **3**, which became immediately colorless. After 5 min, a 1:1 mixture of AcOH and THF (4 mL) was added at − 78°C. Workup gave a mixture of *endo*-**8f** (single diastereomer) and *exo*-**8f** (single diastereomer) (62 mg, 88%) in a ratio of 88:12 (GC) as a colorless solid.

***endo*-8f:** GC: t_R = 12.93 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (dm, $J_{7s,7a}$ = 9.0 Hz, 1 H, H-7_s), 1.18 (dm, $J_{7a,7s}$ = 9.0 Hz, 1 H, H-7_a), 2.91 (s, 1 H, H-4), 3.63 (s, 1 H, H-1), 4.26 (d, $J_{OH,H}$ = 5.0 Hz, 1 H, OH), 5.47 (s, 1 H, H-$8_{a,s}$), 5.49 (m, 1 H, H-5), 5.67 (s, 1 H, H-$8_{a,s}$), 5.83 (d, $J_{H,OH}$ = 5.0 Hz, 1 H, CH), 6.19 (m, 1 H, H-6), 7.29 (m, 3 H, H-12, H-11,13, CPh), 7.41 (tm, 2 H, H-11,13), 7.49 (dm, 2 H, H-10,14, CPh), 7.54 (tm, 1 H, H-12), 7.86 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.54 (C-1), 48.75 (C-7), 51.77 (C-4), 76.52 (CHOH), 85.01 (C-2), 114.06 (C-8), 127.76 (C-11,13), 127.79 (C-10,14), 128.11 (C-12), 128.62 (C-11,13, C*Ph*), 131.04 (C-10,14, C*Ph*), 133.25 (C-5), 138.35 (C-6), 138.47 (C-12, C*Ph*), 139.81 (C-9), 141.07 (C-9, C*Ph*), 145.18 (C-3).

***exo*-8f:** GC: t_R = 12.82 min (DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.48 (dm, $J_{7,7}$ = 9.0 Hz, 1 H, H-$7_{a,s}$), 0.95 (dm, $J_{7,7}$ = 9.0 Hz, 1 H, H-$7_{a,s}$), 2.99 (s, 1 H, H-4), 3.27 (sm, 1 H, H-1), 5.00 (d, $J_{OH,H}$ = 2.3 Hz, 1 H, OH), 5.57 (s, 1 H, H-$8_{a,s}$), 5.72 (s, 1 H, H-$8_{a,s}$), 5.90 (d, $J_{H,OH}$ = 2.3 Hz, 1 H, CH), 6.06 (m, 2 H, H-5, H-6).

***endo*-8f/*exo*-8f:** $C_{21}H_{20}O_3S$ (352.4): calcd. C 71.57, H 5.72; found C 71.41, H 5.76.

(±)-3-[(2-Hydroxy-2-phenyl)ethyl]-2-(phenylsulfonyl)bicyclo-[2.2.1]hepta-2,5-diene (γ-8f): Freshly distilled PhCHO (0.2 mL, 2.0 mmol) was added to solution of **3**, which became immediately colorless. After warming the solution to room temp., it turned yellow again. Workup gave γ-**8f** (51 mg, 72%) as a mixture of diastereomers in a ratio of 50:50 (GC) as a colorless oil.

γ-8f (Diastereomer 1): GC: t_R = 24.46 min (β−CD, 140°C, isotherm, 60 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (dm, $J_{7a,7s}$ = 6.7 Hz, 1 H, H-7_a), 2.04 (m, 1 H, H-7_s), 2.67 (s, 1 H, OH), 3.16 (dd, ^2J = 13.4, ^3J = 7.7 Hz, 1 H, CH_2), 3.26 (dd, ^2J = 13.4, ^3J = 4.7 Hz, 1 H, CH_2), 3.42 (sm, 1 H, H-4), 3.64 (sm, 1 H, H-1), 5.02 (m, 1 H, CH), 6.48 (m, 2 H, H-5, H-6), 7.30 (m, 1 H, H-12, CPh), 7.36 (tm, 2 H, H-11,13, CPh), 7.43 (dm, 2 H, H-10,14, CPh), 7.50 (tm, 2 H, H-11,13), 7.58 (tm, 1 H, H-12), 7.78 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.11 (C-7), 52.37 (C-4), 57.60 (C-1), 71.02 (CH_2), 72.52 (CHOH), 125.79 (C-10,14), 127.42 (C-11,13), 127.76 (C-12), 128.50 (C-10,14, C*Ph*), 129.11 (C-11,13, C*Ph*), 133.12 (C-12, C*Ph*), 139.57 (C-2), 139.93 (C-5), 142.52 (C-6), 143.59 (C-9), 147.89 (C-9, C*Ph*), 166.68 (C-3).

γ-8f (Diastereomer 2): GC: t_R = 24.59 min (β−CD, 140°C, isotherm, 60 kPa H_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.88 (dm, $J_{7a,7s}$ = 6.7 Hz, 1 H, H-7_a), 2.07 (m, 1 H, H-7_s), 2.67 (s, 1 H, OH), 3.06 (dd, ^2J = 13.4, ^3J = 4.7 Hz, 1 H, CH_2), 3.31 (dd, ^2J = 13.4, ^3J = 8.3 Hz, 1 H, CH_2), 3.56 (sm, 1 H, H-4), 3.64 (sm, 1 H, H-1), 4.95 (m, 1 H, CH), 6.48 (m, 2 H, H-5, H-6), 7.30 (m, 1 H, H-12, CPh), 7.36 (tm, 2 H, H-11,13, CPh), 7.43 (dm, 2 H, H-10,14, CPh), 7.50 (tm, 2 H, H-11,13), 7.58 (tm, 1 H, H-12), 7.75 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.04 (C-7), 52.37 (C-4), 57.53 (C-1), 71.48 (CH_2), 73.14 (CHOH), 125.79 (C-10,14), 127.28 (C-11,13), 127.76 (C-12), 128.52 (C-10,14, C*Ph*), 129.11 (C-11,13, C*Ph*), 133.08 (C-12, C*Ph*), 139.82 (C-2), 140.27 (C-5), 142.48 (C-6), 143.88 (C-9), 147.89 (C-9, C*Ph*), 167.01 (C-3).

γ-8f (Mixture of Diastereomers): $C_{21}H_{20}O_3S$ (352.4): calcd. C 71.57, H 5.72; found C 71.66, H 5.96.

(±)-3-[(2-Hydroxy-2-phenyl)ethyl]-2-(phenylsulfonyl)bicyclo-[2.2.1]hept-2-ene (γ-9f) and (±)-*endo*-2-[(1-Hydroxy-1-phenyl)-methyl]-3-methylene-2-(phenylsulfonyl)bicyclo-[2.2.1]-heptane (*endo*-9f): Freshly distilled PhCHO (0.2 mL, 2.0 mmol) was added to the solution of **4**, which became immediately colorless. After 5 min, a 1:1 mixture of AcOH and THF (4 mL) was added to the solution at −78°C. Workup gave a mixture of γ-**9f** (diastereomer 1), γ-**9f** (diastereomer 2) and *endo*-**9f** (only one diastereomer) (56 mg, 79%) in a ratio of 87:10:3 (GC) as a colorless solid.

γ-9f (Diastereomer 1): GC: t_R = 15.31 min (DB-5, *S1*).

γ-9f (Diastereomer 2): GC: t_R = 15.38 min (DB-5, *S1*).

***endo*-9f:** GC: t_R = 15.55 min (DB-5, *S1*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (dm, 1 H, H-7_s), 2.49 (m, 2 H, H-1, H-6), 3.20 (sm, 1 H, H-4), 4.40 (d, $J_{OH,H}$ = 2.2 Hz, 1 H, OH), 4.97 (s, 1 H, H-8_a), 5.30 (s, 1 H, H-8_s), 8.11 (dm, 2 H, H-10,14).

γ-9f (Mixture of Diastereomers)/*endo*-9f: $C_{21}H_{22}O_3S$ (354.5): calcd. C 71.16, H 6.26; found C 70.89, H 6.24.

(±)-3-[(2-Hydroxy-2-phenyl)ethyl]-2-(phenylsulfonyl)bicyclo-[2.2.1]hept-2-ene (γ-9f): Freshly distilled PhCHO (0.2 mL, 2.0 mmol) was added to the solution of **4**, which became immediately colorless. After warming the solution to room temp., it turned yellow again. Workup gave γ-**9f** (47 mg, 66%) as a mixture of diastereomers in a ratio of 69:31 (GC) as a colorless oil.

γ-9f (Diastereomer 1): GC: t_R = 15.28 min (DB-5, *S1*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, H-$7_{a,s}$), 1.04 (m, 1 H, H-5), 1.12 (m, 1 H, H-6), 1.36 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, H-$7_{a,s}$), 1.63 (m, 2 H, H-6, H-5), 2.67 (s, 1 H, H-4), 2.93 (dd, ^2J = 13.4, ^3J = 7.3 Hz, 1 H, CH_2), 3.01 (sm, 1 H, H-1), 3.05 (sm, 1 H, OH), 3.38 (dd, ^2J = 13.4, ^3J = 4.7 Hz, 1 H, CH_2), 5.06 (ddm, ^3J = 7.3, ^3J = 4.3 Hz, 1 H, CH), 7.30 (tm, 1 H, H-12, CPh), 7.36 (tm, 2 H, H-11,13, CPh), 7.44 (dm, 2 H, H-10,14, CPh), 7.51 (tm, 2 H, H-11,13), 7.59 (tm, 1 H, H-12), 7.82 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.77 (C-5), 26.19 (C-6), 37.72 (C-7), 44.97 (C-4), 47.42 (CH_2), 49.77 (C-1), 72.77 (CHOH), 125.77 (C-10,14), 127.38 (C-11,13), 127.69 (C-12), 128.50 (C-10,14, C*Ph*), 129.11 (C-11,13, C*Ph*), 133.20 (C-12, C*Ph*), 140.45 (C-9), 141.33 (C-9, C*Ph*), 143.94 (C-2), 159.17 (C-3).

γ-9f (Diastereomer 2): GC: t_R = 15.36 min (DB-5, *S1*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, H-$7_{a,s}$), 1.15 (m, 1 H, H-5), 1.19 (m, 1 H, H-6), 1.46 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, H-$7_{a,s}$), 1.71 (m, 2 H, H-5, H-6), 2.69 (dd, ^2J = 13.4, ^3J = 4.3 Hz, 1 H, CH_2), 2.86 (dm, 1 H, OH), 2.91 (m, 1 H, H-4), 3.07 (sm, 1 H, H-1), 3.49 (dd, ^2J = 13.4, ^3J = 9.4 Hz, 1 H, CH_2), 4.95 (ddm, ^3J = 9.4, ^3J = 4.3 Hz, 1 H, CH), 7.30 (tm, 1 H, H-12, CPh), 7.36 (tm, 2 H, H-11,13, CPh), 7.44 (dm, 2 H, H-10,14, CPh), 7.51 (tm, 2 H, H-11,13), 7.59 (tm, 1 H, H-12), 7.87 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.66 (C-5), 26.10 (C-6), 37.72 (C-7), 44.97 (C-4), 47.64 (CH_2), 49.14 (C-1), 73.09 (CHOH), 125.83

(C-10,14), 127.38 (C-11,13), 127.78 (C-12), 128.59 (C-10,14, C*Ph*), 129.24 (C-11,13, C*Ph*), 133.20 (C-12, C*Ph*), 140.39 (C-9), 141.33 (C-9, C*Ph*), 144.32 (C-2), 159.51 (C-3).

γ-9f (Mixture of Diastereomers): $C_{21}H_{22}O_3S$ (354.5): calcd. C 71.16, H 6.26; found C 70.89, H 6.28.

(±)-2-(Phenylsulfonyl)-3-[(trimethylsilyl)methyl]bicyclo-[2.2.1]hepta-2,5-diene (γ-8g): Neat Me_3SiCl (0.13 mL, 1.0 mmol) was added to the solution of **3**, whose color did not change. The solution was stirred for 30 min at −78°C and then warmed slowly to −35°C, whereby it became colorless. Workup gave γ-**8g** contaminated only by traces of *endo*-**8g** and *exo*-**8g** (55 mg, 86%) as a colorless oil. − GC: > 95% (t_R = 13.36 min, DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 1.87 (dm, $J_{7a,7s}$ = 6.7 Hz, 1 H, H-7_a), 2.05 (dm, $J_{7s,7a}$ = 6.7 Hz, 1 H, H-7_s), 2.20 (d, ^2J = 11.4 Hz, 1 H, CH_2), 2.60 (d, ^2J = 11.4 Hz, 1 H, CH_2), 3.44 (sm, 1 H, H-1), 3.63 (sm, 1 H, H-4), 6.50 (sm, 2 H, H-5, H-6), 7.49 (tm, 2 H, H-11,13), 7.55 (tm, 1 H, H-12), 7.79 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.69 ($SiMe_3$), 23.63 (CH_2), 51.89 (C-1), 58.92 (C-4), 69.69 (C-7), 127.21 (C-11,13), 128.93 (C-10,14), 132.64 (C-12), 138.77 (C-6), 139.34 (C-9), 140.77 (C-3), 143.44 (C-5), 170.55 (C-2). − GC MS; *m/z* (%): 319 [M^+ + 1] (3), 303 (1), 177 (2), 105 (8), 89 (100), 75 (3), 61 (48). − $C_{17}H_{22}O_2SSi$ (318.5): calcd. C 64.11, H 6.96; found C 64.30, H 6.87.

(±)-2-(Phenylsulfonyl)-3-[(trimethylsilyl)methyl]bicyclo[2.2.1]hept-2-ene (γ-9g): Neat Me_3SiCl (0.13 mL, 1.0 mmol) was added to the solution of **4**, which became light yellow. After stirring the solution for 30 min at −78°C, it became colorless. Workup gave γ-**9g** (51 mg, 80%) as a colorless oil. − GC: 100% (t_R = 14.26 min, DB-5, *S2*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 0.87 (m, 1 H, H-5 or H-6), 1.08 (m, 1 H, H-5 or H-6), 1.11 (dm, $J_{7a,7s}$ = 8.7 Hz, 1 H, H-7_a), 1.47 (dm, $J_{7s,7a}$ = 8.7 Hz, 1 H, H-7_s), 1.55 (m, 1 H, H-5 or H-6), 1.69 (m, 1 H, H-5 or H-6), 1.90 (d, ^2J = 11.4 Hz, 1 H, CH_2), 2.70 (d, ^2J = 11.4 Hz, 1 H, CH_2), 2.76 (sm, 1 H, H-1), 3.06 (sm, 1 H, H-4), 7.50 (tm, 2 H, H-11,13), 7.57 (tm, 1 H, H-12), 7.88 (dm, 2 H, H-10,14). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.66 ($SiMe_3$), 21.03 (CH_2), 24.85 (C-6), 26.68 (C-5), 44.53 (C-1), 46.81 (C-7), 51.03 (C-4), 127.20 (C-11,13), 129.00 (C-10,14), 132.69 (C-12), 132.90 (C-9), 142.61 (C-3), 163.52 (C-2). − GC MS; *m/z* (%): 321 [M^+ + 1] (3), 305 (31), 277 (2), 199 (2), 135 (1), 89 (100), 75 (3), 61 (39). − $C_{17}H_{24}O_2SSi$ (320.5): calcd. C 63.70, H 7.55; found C 63.79, H 7.48.

In Situ Methylation of Lithiosulfones 3 and 4 − (±)-*endo*- and (±)-*exo*-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-8b and *exo*-8b): Neat MeI (0.14 mL, 2.2 mmol) was added at −78°C (−105°C) to a solution of *endo*-**5** or *exo*-**5** (50 mg, 0.2 mmol) in THF (5 mL). Subsequently, the solution was treated dropwise with *n*BuLi (0.14 mL, 1.6 M in *n*-hexane, 0.22 mmol) at this temp., whereby it remained colorless. Stirring of the mixture was continued at −78°C (−105°C) for 10 min. Workup gave a mixture of *endo*-**8b** and *exo*-**8b** (50 mg, 96%) in a ratio of 76:24 (68:32 or 57:43) (GC) as a colorless solid.

(±)-*endo*- and (±)-*exo*-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (*endo*-9b and *exo*-9b): Neat MeI (0.14 mL, 2.2 mmol) was added at −78°C (−105°C) to a solution of *endo*-**6** or *exo*-**6** (50 mg, 0.2 mmol) in THF (5 mL). Subsequently, the mixture was treated dropwise with *n*BuLi (0.14 mL, 1.6 M in *n*-hexane, 0.22 mmol) at this temp., whereby it remained colorless at −78°C but became transient yellow at −105°C. Stirring was continued for 10 min at −78°C (−105°C). Workup gave a mixture of *endo*-**9b** and *exo*-**9b** (50 mg, 95%) in a ratio of 80:20 (80:20 or 81:19) (GC) as a colorless solid.

Partial Hydrogenation of (±)-*endo*- and (±)-*exo*-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene: A mixture of *endo*-**8b** and *exo*-**8b** (88 mg, 0.34 mmol) in a ratio of 76:24 and 10% Pd/C (200 mg) in MeOH (30 mL) was vigorously stirred under H_2 at room temp. After 5 min, the theoretical amount of H_2 had been consumed and hydrogenation was terminated by the removal of the catalyst by filtration through Celite. Concentration of the solution in vacuo gave a mixture of *endo*-**9b** and *exo*-**9b** (76 mg, 86%) in a ratio of 76:24 (GC) as a colorless solid.

H/D Exchange of Sulfones *exo*-5, *endo*-5, *exo*-6 and *endo*-6: A solution of CD_3ONa (0.005 mmol) in CD_3OD (0.1 mL) was added at 25°C to a solution of sulfone (0.2 mmol) in CD_3OD (0.7 mL), contained in a NMR tube, and ^{1}H-NMR spectra were recorded after the time given in Tables 10−13.

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[21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102801 and CCDC-102802. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk).

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