Lithium Salts of Conformationally Constrained and Restricted Chiral Allylic α-Sulfonyl Carbanions − A Joint Study of their Structures, Dynamics, and Stereoselectivities

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The structures of the lithium salts of the chiral bicyclic allylic α-sulfonyl carbanions **3**–**5**, each possessing a norbornane skeleton and a *tert*-butyl group at the S atom, have been studied by ^{1}H, ^{13}C, ^{6}Li, and ^{6}Li,^{1}H HOESY NMR spectroscopy, cryoscopy, and X-ray crystal structure analysis. Because of their relatively high *endo*-*exo* isomerization barriers, the Cα–S *endo* and *exo* diastereomers of **3**–**5** could be observed by NMR spectroscopy at –30 °C to –50 °C in [D$_8$]THF. The *endo* diastereomer is the preferred equilibrium species under these conditions, as shown by ^{1}H,^{1}H HOESY experiments. Carbanion salt **3** has *endo*-*exo* isomerization barriers of $\Delta G^{\#}_{270}$ = 13.1±0.1 kcal/mol and 12.6±0.1 kcal/mol, while the 7-benzhydrylidene-substituted carbanion salt **5** has barriers of $\Delta G^{\#}_{288}$ = 13.5±0.1 kcal/mol and 13.3±0.1 kcal/mol. Cryoscopy and ^{6}Li NMR spectroscopy of **5** in THF at –100 °C to –108 °C revealed the formation of dimers and monomers in a ratio of approximately 2:1. NMR spectroscopy of **3**–**5** at –90 °C to –105 °C allowed observation of the dimers and monomers of which the anions have *endo* conformations and also of which the anions adopt *exo* conformations. The NMR spectroscopic results for **3**–**5** are compatible with monomeric and dimeric CIPs, featuring planar allylic moieties and allylic stabilization by delocalization of the negative charge. ^{6}Li,^{1}H-HOESY examination of the mixture of the monomers and dimers of *endo*-**5** and *exo*-**5** in [D$_8$]THF at room temperature gave only evidence for coordination of the Li atom to the O atom(s) in the CIPs. The NMR spectroscopic results for **3** were corroborated by X-ray crystal structure analysis of the monomer *exo*-**3**·PMDETA, which features (i) an essentially planar anionic C(2) atom, (ii) the *exo* conformation, (iii) the typical Cα–S conformation, also allowing for a stabilizing n_C–σ^*_{StBu} interaction, and (iv) a single O–Li bond, but no C–Li bond. Upon treatment of the *endo* and *exo* sulfones **9**, **10**, and **12** with *n*BuLi at very low temperatures, the corresponding *endo* and *exo* carbanion salts *endo*-**3**–**5** and *exo*-**3**–**5**, respectively, were selectively generated as mixtures of monomers and dimers, the reactions of which with electrophiles were studied. Deprotonation of the *exo* and *endo* sulfones with *n*BuLi proceeds stereoselectively, the *exo* sulfone preferentially giving the *endo* anion and vice versa. The diastereomeric *endo* and *exo* carbanion salts **3**–**5** each react with reactive electrophiles at the anionic C(2) atom *syn* to the sulfonyl O atoms, giving the corresponding substituted *endo* and *exo* sulfones, respectively, with significant degrees of asymmetric induction. Reactions of the *endo* and *exo* diastereomers of **3**–**5** with CF$_3$COOD and MeOCH$_2$I were faster than their *endo*-*exo* isomerization and approached kinetic quenching, while those with MeI and allyl iodide were slower, approaching the Curtin–Hammett limit and preferentially giving the *exo* sulfones. Deprotonation-deuteration experiments of the 7-oxa-sulfone *endo*-**11** showed that the corresponding 7-oxa-substituted carbanion salts *endo*-**6** and *exo*-**6** not only can be generated at low temperatures but may also, despite their tendency to rearrange, be converted into the corresponding 7-oxa-sulfones on treatment with reactive electrophiles.

Introduction

Lithium salts of allylic α-sulfonyl carbanions **I** (Figure 1) have found many applications in organic synthesis.[1,2] This is because of their ready reaction with electrophiles at the α- and/or γ-positions and the synthetic versatility of the vinylic and allylic sulfones produced. Knowledge of the structures of **I**, in contrast, is not commensurate with their synthetic importance,[3−6] and it is only recently that further attempts to close the gap have been made.[7−9] Studies of the structures of **I** in solution are complicated not only by the existence of conformational and aggregational equilibria, but also by the possible formation of different contact ion pairs (CIPs). In particular, the nature of the cation-anion interaction in the CIPs of **I**, which may have important bearings upon regioselectivity, is still obscure.[9] Experimental observation of the different conformers, aggregates, and CIPs of **I** in solution has so far been precluded by their fast equilibration even at low temperatures.[7−9] A particularly interesting aspect of **I** is their chirality, which has its origin in the preferred Cα−S conformation of the anion, shown by formulas **II** and *ent*-**II**.[4] This feature has apparently been ignored up to now despite the considerable potential it could hold for stereoselective synthesis. For example, nothing is known about the height of the enantiomerization barrier (**II** → *ent*-**II**) and about whether the sulfonyl group exerts, as in non-allylic α-sulfonyl carbanions,[10] any significant asymmetric induc-

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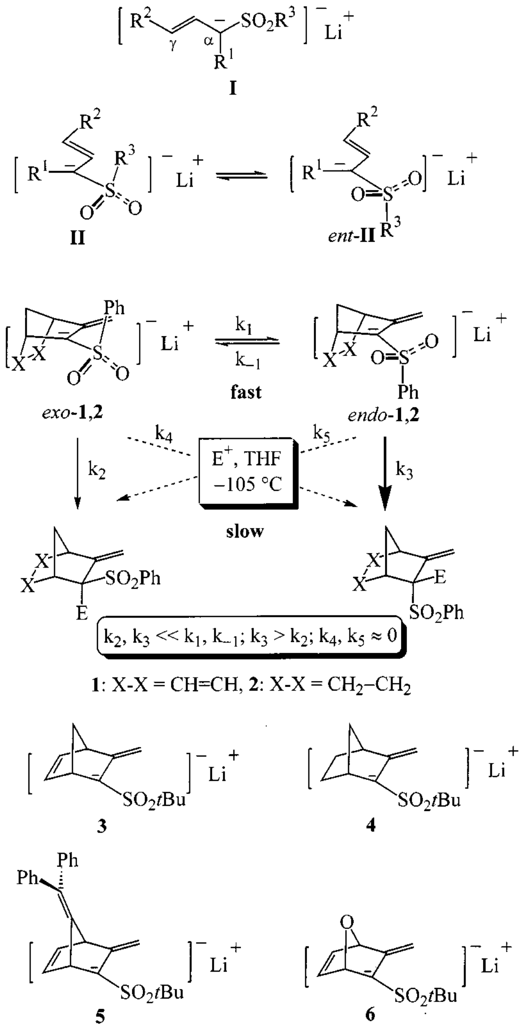


Figure 1. Lithium salts of acyclic and bicyclic allylic α-sulfonyl carbanions.

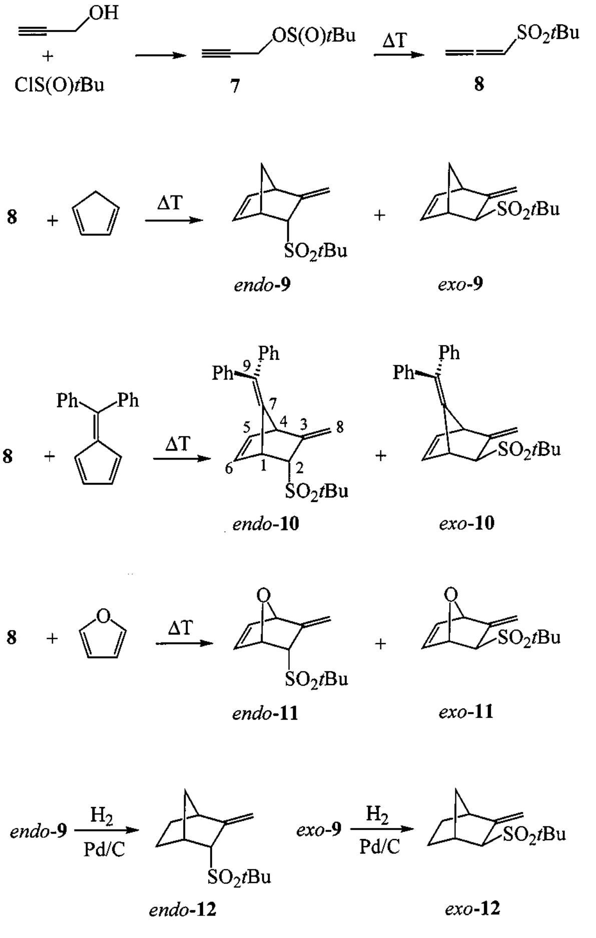
tion in reactions with electrophiles at the α- and γ-positions. We recently reported a study of the bicyclic allylic carbanion salts **1** and **2**, in which we addressed their structures, conformational stabilities, and stereoselectivities by a combination of experimental and computational methods.[7] Carbanion salts **1** and **2** had been selected as probes for **II** and *ent*-**II** because of their constrained s-*cis* Cα−Cβ conformations and their allylic moieties, being embedded in the unsymmetrical norbornane skeletons. These features not only result in a reduction in the number of possible conformers, but also provide for the existence of diastereomeric rather than enantiomeric Cα−S conformers with either the *endo* or the *exo*[11] conformations. Finally, the *cis* positions of the sulfonyl groups and the allylic double bonds should favor CIPs of **1** and **2** with C−Li bonds as well as O−Li bonds. It was found that, in THF solution, carbanion salts **1** and **2** form monomeric and dimeric CIPs, which adopt the *endo* and the *exo* Cα−S conformations. X-ray crystal structure analysis of diglyme-solvated dimers of **1** and **2** revealed CIPs that featured *endo* conformations and possessed only O−Li bonds, with no C−Li bonds (vide infra). Surprisingly, the anionic Cα atoms of the dimers of **1** and **2** are not planar, but strongly pyramidalized in the *exo* direction. Determination of the structures of monomeric **1** and **2** in the crystal could not be achieved because of failure to isolate such species. This would have been very desirable, since knowledge of the structures of monomeric lithium salts of α-sulfonyl carbanions in the crystal is scant.[12] NMR spectroscopy of **1** and **2** in THF showed the *endo* and *exo* diastereomers, as well as the monomers and dimers, to be in rapid equilibrium even at very low temperatures. As a consequence, the diastereomers and aggregates could not be studied individually and only averaged structural information was obtained. The reactions of **1** and **2** with all electrophiles studied preferentially yielded the corresponding α-substituted *endo* sulfones. This was explained on the basis of the Curtin−Hammett (C−H) principle[13] (k_2, $k_3 << k_1$, k_{-1}), by proposing that the *endo* diastereomers reacted with electrophiles more readily from the *exo* side than the *exo* diastereomers from the *endo* side ($k_3 > k_2$), because of smaller degrees of eclipsing of newly formed and existing bonds in the *exo* transition states (TS) (*cf.* Figure 1).[7] A further important assumption made was that the sulfonyl groups of *endo* and *exo* **1** and **2** directed electrophiles to attack the Cα atoms with high selectivities from the side *syn* to the O atoms and thereby suppressed crossover reactions (k_4, $k_5 \approx 0$). Unfortunately, however, kinetic quenching (k_2, $k_3 >> k_1$, k_{-1})[13b] of the *endo* and *exo* diastereomers of **1** and **2**, which would have given important clues as to the validity of these assumptions, was not possible because of their fast equilibration. In the light of the problems associated with the fast *endo*-*exo* isomerization of **1** and **2**, it was decided to investigate the analogous carbanion salts **3** and **4**, which bear the sterically more demanding *tert*-butyl group at the S atom. Since lithium salts of chiral acyclic α-*tert*-butylsulfonyl carbanions had been found to display significantly higher enantiomerization barriers than their *S*-phenyl analogs,[10] it was hoped that the *endo* and *exo* diastereomers of **3** and **4** would also possess isomerization barriers significantly higher than those of **1** and **2**. This should aid not only in investigation of their structures and dynamics, but also allow for the determination of their stereoselectivities through kinetic quenching. Further goals of the investigation of **3** and **4** were the determination of the structures of their monomers and dimers in solution and of their monomers in the crystal. In order to study the influence of the methylene group in the 7-position upon the structure and dynamics of **3**, carbanion salt **5**, which bears a benzhydrylidene group at C(7), and carbanion salt **6**, with an O atom in the 7-position,[14] were included in this investigation.

Here we report on studies of the allylic *S*-*tert*-butylsulfonyl carbanion salts **3**−**6**, which provided (i) NMR spectroscopic observation of the Cα−S diastereomers, monomers, and dimers in solution, (ii) estimations of the conformational barriers, (iii) the determination of the crystal structure of a monomer, and (iv) estimations of the stereoselectivities of the *endo* and *exo* diastereomers.[15]

Results and Discussion

1. Syntheses and Structures of the Bicyclic *tert*-Butyl Sulfones

Treatment of propargyl alcohol with *tert*-butylsulfinyl chloride[16] gave the sulfinyl ester **7** in 92% yield (Scheme 1). Rearrangement[17] of ester **7** in refluxing chlorobenzene afforded the allene **8** in 67% yield, as light yellow crystals. A Diels–Alder reaction[17] between **8** and cyclopentadiene in refluxing toluene furnished a 1.4:1 mixture of the allylic sulfones *endo*-**9** and *exo*-**9**. Chromatography and crystallization gave *endo*-**9** in 43% yield and *exo*-**9** in 41% yield (based on **8**), both as colorless crystals. Treatment of **8** with diphenylfulvene in refluxing toluene afforded a 2.6:1 mixture of the 7-benzhydrylidene-sulfones *endo*-**10** and *exo*-**10**, in 72% yield. Samples of the pure *exo* and *endo* diastereomers were obtained by HPLC. Treatment of **8** with furan in refluxing toluene, followed by chromatography and crystallization of the crude product, furnished the 7-oxa-sulfone *endo*-**11** in 61% yield as colorless crystals, together with a 2:1 mixture of *endo*-**11** and *exo*-**11** in 12% yield. The norbornyl sulfones *endo*-**12** and *exo*-**12** were obtained in 75% and 60% yields, respectively, through selective hydrogenation[17b] of *endo*-**9** and *exo*-**9**.



Scheme 1. Synthesis of the bicyclic *tert*-butyl sulfones **9**–**12**.

Base-catalyzed equilibration of sulfones *exo*-**9** and *endo*-**9** with $NaOCD_3$ in CD_3OD in both cases gave a mixture of the *exo* and *endo* isomers, both fully deuterated at their α-positions (>98% D), in a ratio of 67:33. Thus, the *exo* isomer is, as in the case of the corresponding *S*-phenyl derivative,[7] more stable than the *endo* isomer.

The configuration of sulfone *exo*-**9** was determined by X-ray crystal structure analysis (Figure 2).[18] The bonding parameters of *exo*-**9** are in the normal range and show no peculiarities (Table 1).[7,19] Presumably for steric reasons, *exo*-**9** adopts a C(2)–S conformation in which the *tert*-butyl group is gauche to 2-H and approximately *anti* to C(3) as indicated by the values of the dihedral angles C(9)–S–C(2)–H(2), C(9)–S–C(2)–C(3), and C(9)–S–C(2)–C(1).

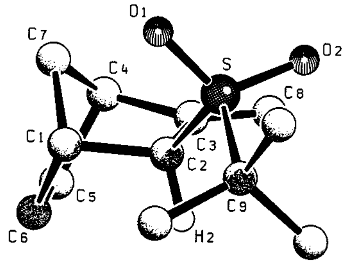


Figure 2. Structure of *exo*-**9** in the crystal.

Table 1. Selected bond lengths (Å) and bond angles (°) of sulfone *exo*-**9**, carbanion salt *exo*-**3**·PMDETA, and sulfone *exo*-**13c**.

Bond/angle	*exo*-**9**	*exo*-**3**·PMDETA	*exo*-**13c**
S–C(2)	1.829(4)	1.626(5)	1.851(4)
S–C(9)	1.832(5)	1.828(5)	1.832(5)
S–O(1)	1.442(4)	1.461(3)	1.434(4)
S–O(2)	1.437(4)	1.473(3)	1.439(4)
C(2)–C(3)	1.528(7)	1.442(7)	1.542(6)
C(3)–C(8)	1.289(8)	1.349(7)	1.311(7)
C(5)–C(6)	1.327(8)	1.294(8)	1.309(8)
O(1)–Li(1)	–	–	–
O(2)–Li(1)	–	1.850(8)	–
C(1)–C(2)–C(3)	101.6(3)	106.0(4)	100.1(4)
C(1)–C(2)–S	113.6(3)	123.3(3)	114.6(3)
C(3)–C(2)–S	112.9(3)	130.4(4)	105.5(3)
C(2)–C(3)–C(4)	104.7(4)	103.1(4)	105.4(4)
C(2)–C(3)–C(8)	126.8(4)	133.6(5)	126.6(4)
O–S–O	117.0(2)	116.0(2)	116.6(3)
C(9)–S–C(2)–C(10)	–	–	72.4(3)
C(9)–S–C(2)–H(2)	−23.6(4)	–	–
C(9)–S–C(2)–C(1)	98.6(4)	92.4(4)	−57.0(4)
C(9)–S–C(2)–C(3)	−146.4(4)	−95.0(5)	−166.1(3)
S–C(2)–C(3)–C(8)	59.7(7)	2.4(9)	−64.9(5)

On the basis of the unequivocal determination of the configuration of *exo*-**9**, assignment of the signals in the NMR spectra of *endo*-**9**, *exo*-**9**, *endo*-**10**, *exo*-**10**, *endo*-**11**, *exo*-**11**, *endo*-**12**, and *exo*-**12** was accomplished with the aid of NOE experiments and two-dimensional methods ($^1H,^1H$ COSY, $^{13}C,^1H$ COSY) (Table 2 and Table 3). The signs of the Δδ (^1H) values for 7-H_{syn} and 2-H, on going from the *endo* to the *exo* isomers, are the same as those found for the

Table 2. ^{1}H NMR spectroscopic data (δ, ppm) of sulfones **9**−**12** in $CDCl_3$ at 25 °C.

Atom	*endo*-**9**	*exo*-**9**	*endo*-**10**	*exo*-**10**	*endo*-**11**	*exo*-**11**	*endo*-**12**	*exo*-**12**
1-H	3.33	3.30	3.82	3.79	5.24	5.43	2.85	2.82
2-H	4.24	3.57	4.43	3.73	4.37	3.60	4.00	3.57
4-H	3.33	3.39	3.89	3.96	5.14	5.20	2.80	2.87
5-H_{exo}	6.29	6.18	6.52	6.44	6.62	6.58	1.72	1.72
5-H_{endo}	–	–	–	–	–	–	1.57	1.40
6-H_{exo}	6.29	6.35	6.52	6.54	6.57	6.43	1.48	1.72
6-H_{endo}	–	–	–	–	–	–	2.35	1.30
7-H_{syn}	1.55	2.08	–	–	–	–	1.48	1.99
7-H_{anti}	1.69	1.70	–	–	–	–	1.48	1.34
8-H_{syn}	5.28	5.29	5.34	5.55	5.36	5.47	5.43	5.33
8-H_{anti}	5.29	5.39	5.34	5.47	5.37	5.55	5.19	5.22
CMe_3	1.47	1.48	1.43	1.18	1.47	1.48	1.46	1.46

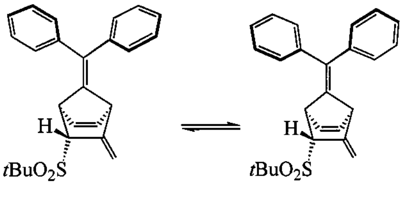
Table 3. ^{13}C NMR spectroscopic data (δ, ppm) of sulfones **9**−**12** in $CDCl_3$ at 25 °C.

Atom	*endo*-**9**	*exo*-**9**	*endo*-**10**	*exo*-**10**	*endo*-**11**	*exo*-**11**	*endo*-**12**	*exo*-**12**
C(1)	46.90	47.59	49.46[a]	47.67[a]	80.36[a]	81.27[a]	41.53	42.27
C(2)	61.80	59.97	61.66	62.96	59.32	64.34	63.53	63.09
C(3)	144.18	143.05	148.94	147.65	139.70	137.92	146.10	146.93
C(4)	51.95	49.62	54.29[b]	52.92[b]	83.94[b]	81.92[b]	46.43	44.26
C(5)	135.30	140.56	134.58[b]	133.72[b]	134.08[b]	134.33[b]	28.48	30.21
C(6)	134.01	134.73	135.99[b]	142.13[b]	135.40[b]	138.23[b]	22.98	27.41
C(7)	49.80	48.19	123.92	126.47	–	–	39.77	37.58
C(8)	110.40	112.42	111.10	112.23	110.88	112.41	109.51	111.76
*C*Me$_3$	60.34	61.07	60.79	61.42	60.34	63.49	60.97	60.88
C*Me*$_3$	23.82	24.06	24.14	24.24	23.62	24.36	24.14	24.13
C(9)	–	–	142.43	139.85	–	–	–	–

[a] C(1) or C(4). – [b] C(5) or C(6).

corresponding *S*-phenyl derivatives of *endo*-**9**, *exo*-**9**, *endo*-**12**, and *exo*-**12**.[7] Because of the anisotropy effect of the sulfonyl group, the signals of 7-H_{syn} in *exo*-**9** and *exo*-**12** are significantly shifted downfield from their counterparts in *endo*-**9** and *endo*-**12**. In the case of *endo*-**9**, *endo*-**10**, *endo*-**11**, and *endo*-**12**, it is the signals of 2-H that are significantly shifted downfield relative to those in *exo*-**9**, *exo*-**10**, *exo*-**11**, and *exo*-**12**. Presumably because of the ring current of the phenyl group in the position *syn* to the sulfonyl group, the signal of the *tert*-butyl group of *exo*-**10** is significantly shifted upfield from that in *endo*-**10**.

Sulfones *endo*-**9**−**12** and *exo*-**9**−**12** can adopt several different diastereomeric Cα−S conformations. In the case of the benzhydrylidene-sulfones *endo*-**10** and *exo*-**10**, two additional diastereomeric conformations, designated as *M* and *P* (Scheme 2), exist because of the two different spatial positions that the phenyl rings can adopt.[20] For the same reason, the number of possible forms of the carbanion salt **5** is doubled in comparison to those of carbanion salts **3**, **4**, and **6**. For the planned NMR spectroscopic investigation of the conformational and aggregational behavior of **5** in solution, it was therefore of considerable importance to obtain an estimate of the height of the isomerization barriers between its *M* and *P* conformers. Sulfone *endo*-**10** was chosen as model for **5** because of the *endo* position of the sulfonyl group, which renders steric interference with the phenyl rings impossible. The ^{1}H and ^{13}C NMR spectra of *endo*-**10** in [D$_8$]THF showed no sign of a line-broadening or splitting of signals down to −90 °C.[21] Thus, equilibration of *M*-*endo*-**10** and *P*-*endo*-**10** is still fast on the NMR timescale at this temperature. This is corroborated by results from previous studies of stereomutation processes involving two phenyl groups bound to the same sp^2-hybridized C-atom.[20] In all cases so far reported, the barriers (in accordance with the results of computational studies) have activation energies so low as to preclude observation of the processes by DNMR spectroscopy. It is therefore assumed that *endo*-**10** also has such low barriers.



M-*endo*-**10** *P*-*endo*-**10**

Scheme 2. Conformers of the benzhydrylidene-sulfone *endo*-**10**.

2. Structure of the Lithium Salts of the Allylic *S*-*tert*-Butylsulfonyl Carbanions

a. Structure in the Crystal

Of particular interest were the crystal structures of the monomers of the carbanion salts **3**−**5**. Whereas the structures of the dimers of **1** and **2**,[7] which may serve as models for those of **3**−**5**, and those of several other lithium salts of α-sulfonyl carbanions in the crystal are known, knowledge of the structure of the corresponding monomers in the crystal is scarce.[12,22] Previous experience with the selective crystallization of monomeric lithium and potassium salts of non-allylic α-sulfonyl carbanions from equilibrating mixtures of monomers and dimers suggested the use of a tri- or tetradentate ligand for the lithium cation.[12,23] Treatment of *endo*-**9** or *exo*-**9** with *n*BuLi in THF solution in the presence of pentamethyldiethylenetriamine (PMDETA) afforded in both cases the carbanion salt *exo*-**3**·PMDETA, containing one PMDETA molecule per formula unit. An X-ray crystal structure analysis of *exo*-**3**·PMDETA revealed a monomeric CIP, the Li atom of which was bound only to one of the two O atoms of the anion and not to the allylic moiety (Figure 3).[18] This mode of coordination between the Li atom and the anion in the CIP renders the S atom chiral. In *exo*-**3**·PMDETA, the Li atom is coordinated to the O atom, which is *syn* to the *exo* cyclic double bond. In this position, which is characterized by an S−O−Li angle of 139.6° and a C(2)−S−O−Li dihedral angle of 90.1°, the Li atom comes spatially close to the exocyclic double bond without the formation of a C−Li bond, however. Perhaps responsible for the absence of such a bond and for the lack of an additional O−Li bond to the second O atom are the steric interactions that would otherwise result between the anion and the tridentate ligand and/or the lack of free coordination sites at the Li-atom.

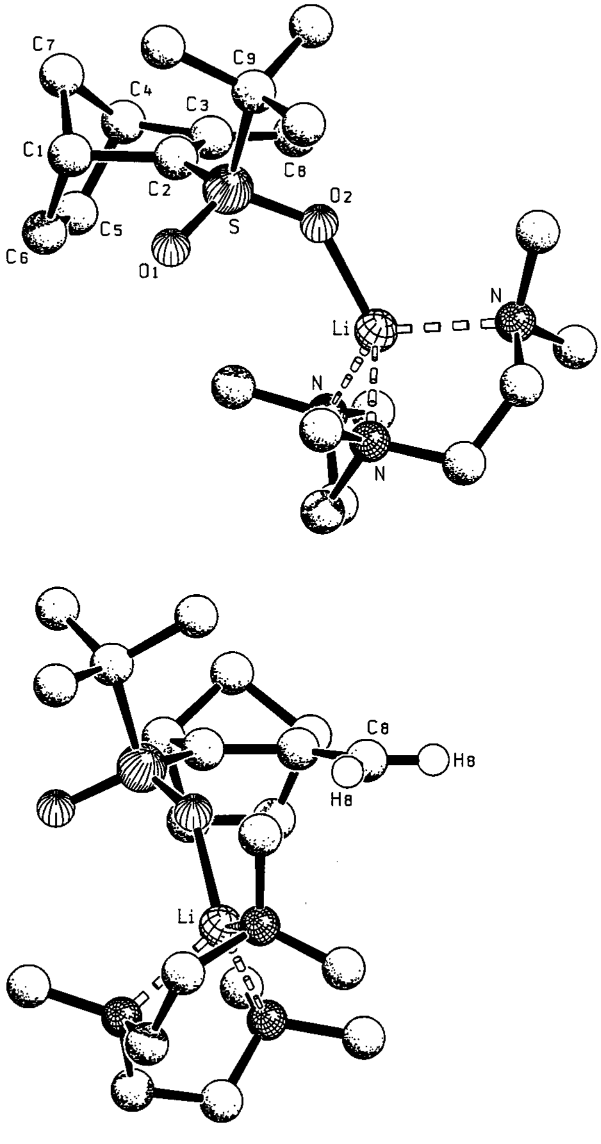
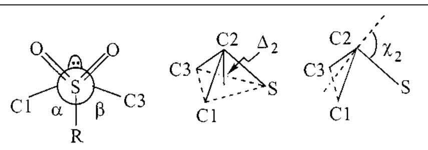


Figure 3. Structure of *exo*-**3**·PMDTA in the crystal.

The anion of *exo*-**3**·PMDETA has the *exo* C(2)−S conformation and the lone pair orbital at C(2) is periplanar to the S−*t*Bu bond. This spatial arrangement of the lone pair orbital and the S−*t*Bu bond, which is typical of α-sulfonyl carbanions,[4,7,9,22,23a] results from a stabilizing hyperconjugative $n_C-\sigma^*_{SR}$ interaction.[24] It should be emphasized, however, that at the same time torsional interactions around the Cα−S bond are minimized in this conformation. Comparison of the bonding parameters of *exo*-**3**·PMDETA with those of the corresponding carbon acid *exo*-**9** shows a significant shortening of the C(2)−S bond and, albeit to a lesser extent, a lengthening of the C(3)−C(8) bond and a shortening of the C(2)−C(3) bond (*cf.* Table 1). Similar differences in bond lengths were observed between *endo*-**1**/*ent*-*endo*-**1** and *endo*-**2**/*ent*-*endo*-**2** and the corresponding sulfones.[7] The shortening of the C(2)−S bond is attributable to a Coulombic interaction between the negative charge at C(2) and the partially positive charged S atom, as well as to the $n_C-\sigma^*_{StBu}$ interaction.[24] According to experiment and theoretical calculations, Coulombic interaction, negative hyperconjugation, and polarization are (in that order) the mechanisms through which a sulfonyl group stabilizes a carbanion. The shortening of the C(2)−C(3) bond and the lengthening of the C(3)−C(8) bond would be compatible both with allylic delocalization of the negative charge and with a Coulombic interaction between C(2) and C(3), stemming from polarization of the C(3)−C(8) double bond by the negative charge localized at C(2)[25] (vide infra). The anionic C(2) atom in *exo*-**3**·PMDETA is essentially planar, as indicated by several planarity criteria (Table 4). This would fit with the picture

Table 4. Coordination geometry of the anionic C atoms of carbanion salts *exo*-**3**·PMDTA, *endo*-**1**/*ent*-*endo*-**1**, and *endo*-**2**/*ent*-*endo*-**2**.



	exo-**3**·PMDETA R = *t*Bu	*endo*-**1**/*ent*-*endo*-**1** R = Ph	*endo*-**2**/*ent*-*endo*-**2** R = Ph
α [°]	92.4(4)[a]	67.2[a]	73.0[a]
β [°]	95.0(5)[a]	73.3[a]	79.5[a]
Σ_2 [°]	359.7	349.8	355.2
Δ_2 Å	0	0.29	0.19
χ_2 [°]	0	35.3	24.0

[a]Absolute value.

of allylic delocalization of the negative charge. In the crystal, the anionic C(2) atoms in the *S*-phenyl-substituted carbanion salts *endo*-**1**/*ent*-*endo*-**1** and *endo*-**2**/*ent*-*endo*-**2** (vide infra) are not planar but significantly pyramidalized in the *exo* direction. Pyramidalization of C(2) of the norbornyl anion of *endo*-**2**/*ent*-*endo*-**2** is smaller in magnitude than that of the norbornenyl anion of *endo*-**1**/*ent*-*endo*-**1**. In the latter two cases, the deviation from planarity of the coordination geometries of the anionic C(2) atoms and the difference in their magnitudes had been ascribed to minimization of strain in the norbornyl and norbornenyl ring systems, which is more important in the latter anion.[7] The lack of pyramidalization of C(2) of *exo*-**3**·PMDETA, compared to that in *endo*-**1**/*ent*-*endo*-**1** and *endo*-**2**/*ent*-*endo*-**2**, might be due to a minimization of steric interactions between the bulky *tert*-butyl group and the methylene group in the 7-position. The different coordination geometries of the anionic C(2) atoms in *exo*-**3**·PMDETA, *endo*-**1**/*ent*-*endo*-**1**, and *endo*-**2**/*ent*-*endo*-**2** are further confirmation of the notion that the difference in energy between a planar and an α-sulfonyl carbanion pyramidalized to a greater or lesser degree is only small.[7,22b,22g] Amongst the lithium salts of allylic α-sulfonyl carbanions the crystal structures of which have been determined,[4,7,8] *exo*-**3**·PMDETA is the only one with an essentially planar Cα-atom.

b. Structure in Solution

Cryoscopy and NMR Spectroscopy: It was found previously that the carbanion salts **1** and **2** both form mixtures of dimers and monomers in THF solution at −108 °C, in ratios of approximately 1:1.[7] In order to examine the aggregation of **3**−**5**, cryoscopic experiments in THF were undertaken. Cryoscopy of the carbanion salt **5** in THF at −108 °C gave an aggregation number $n = 1.73 \pm 0.15$. Thus, this carbanion salt forms an approximately 2:1 mixture of dimers and monomers (vide infra) under these conditions. Since cryoscopy gives only an averaged aggregation number, the existence of higher oligomers of **5**, such as tetramers,[12a] cannot be ruled out. Unfortunately, determination of the aggregation of **3** and **4** in THF by cryoscopy proved impossible[12b] because of the occurrence of two-phase supercooling in both cases.[26,27] However, from the similar aggregational behavior of **1**, **2**, and **5** it seems very likely that carbanions salts **3** and **4** also exist in THF solution as mixtures of monomers and dimers (vide infra). In THF at −108 °C, the analogous acyclic carbanion salts **Ia**, $R^1 = R^2 = H$, $R^3 = Ph$ and **Ib**, $R^1 = R^2 = Et$, $R^3 = t\mathrm{Bu}$, exist mainly as a monomer[9] and as a mixture of a monomer and a dimer in a ratio of 4:1,[8] respectively.

Strong evidence for the existence of a monomer-dimer equilibrium now having been obtained, at least in the case of **5**, variable temperature NMR experiments were carried out on **3**−**5** in order to gain information both about their conformational behavior with regard to the Cα−S bond and about their monomer and dimer natures. Solutions of the carbanion salts **3**−**5** in [D$_8$]THF were prepared by treatment of sulfones **9**, **12**, and **10**, respectively, either as pure diastereomers or as mixtures, with equimolar amounts of *n*BuLi in *n*-hexane at −78 °C, followed by removal of the solvents in vacuo and redissolution of the residue in [D$_8$]THF. Carbanion salt **6** could not be studied by NMR spectroscopy even at low temperatures, because of its rapid rearrangement by ring-opening[17c,28] (vide infra). Only one set of signals was observed in the ^{1}H and ^{13}C NMR spectra (500 MHz and 125 MHz) of **3**−**5** at room temperature in each case (Figure 4−9). This shows that attainment of the monomer-dimer, the *endo*-*exo*, and other possible equilibria of **3**−**5** (Scheme 3) was in each case fast relative to the NMR timescale at this temperature. Assignment of the averaged signals (vide infra) in the ^{1}H and ^{13}C NMR spectra of **3**−**5** at room temperature was accomplished by a combination of two-dimensional methods (^{1}H,^{1}H COSY, ^{13}C,^{1}H COSY) and NOE experiments. On going from the carbon acid to the carbanion salt, shift differences of similar signs and magnitudes were observed for **3**−**5** (Table 5 and Table 6). Similar differences, discussed later, had been observed in the case of **1** and **2** and other lithium salts of acyclic allylic α-sulfonyl carbanions.[3−9,12c]

Although the ^{1}H NMR spectra of **3**−**5** in [D$_8$]THF at room temperature in each case showed only one set of signals (*cf.* Figure 4−6), several signals were already broad and, upon cooling of the solutions of the carbanion salts, a coalescence phenomenon was observed in each case. Several signals of **3**, **4**, and **5** were split at −30 °C to −50 °C, in each case into two, and in ratios of approximately 2.5:1 (−40 °C), 3:1 (−50 °C), and 1.4:1 (−30 °C), respectively. At even lower temperatures these ratios increased. The ^{1}H

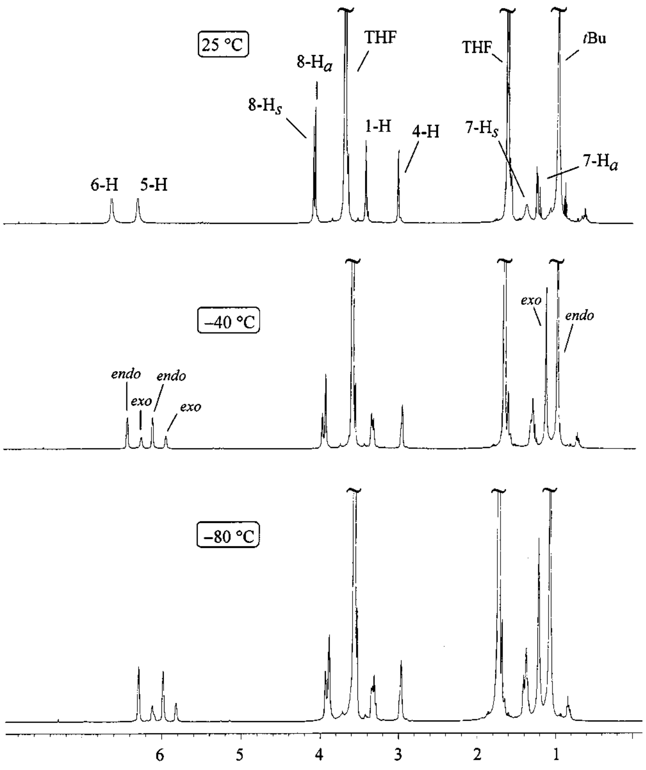


Figure 4. Temperature-dependent ^{1}H NMR spectra (500 MHz) of **3** in [D$_8$]THF.

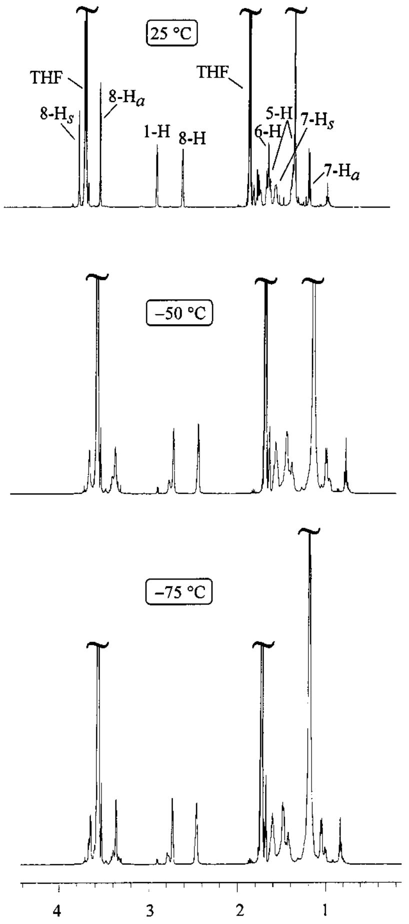


Figure 5. Temperature-dependent ^{1}H NMR spectra (500 MHz) of **4** in [D$_8$]THF.

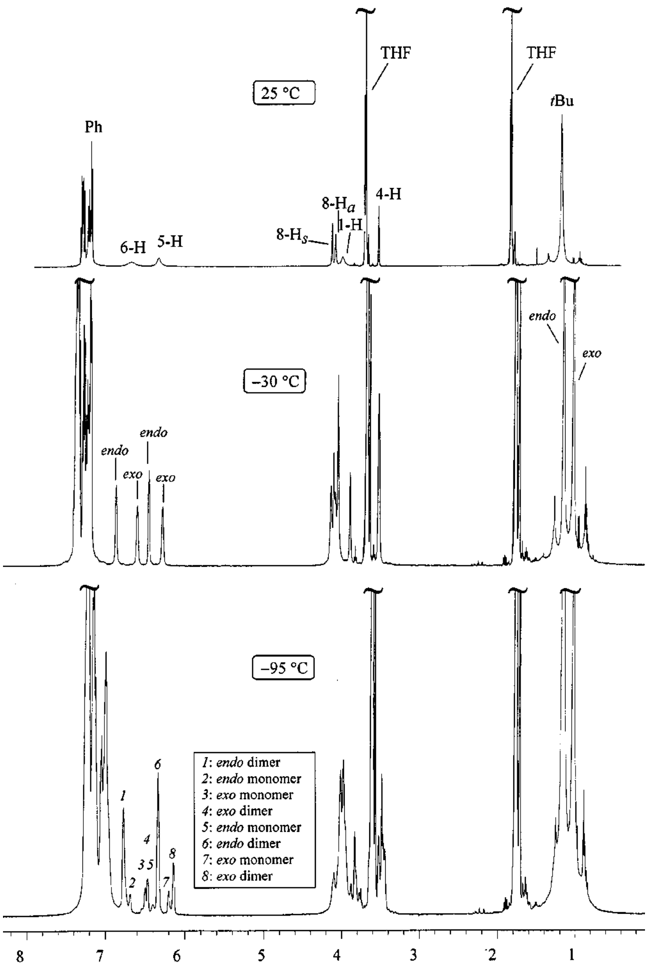


Figure 6. Temperature-dependent ^{1}H NMR spectra (500 MHz) of **5** in [D$_8$]THF.

NMR spectrum of **3** at −40 °C showed a twofold splitting of the signals of 6-H, 5-H, 1-H, 7-H$_{syn}$, and the *tert*-butyl group. The spectrum of **4** at −50 °C exhibited twofold splitting of the signals of 1-H, 8-H$_{anti}$, and 7-H$_{anti}$, and that of **5** at −30 °C was characterized by twofold splitting of the signals of 6-H, 5-H, 8-H, 1-H, and the *tert*-butyl group. In each case the chemical shift differences for the two species of **3**−**5** were only small. The largest observed shift differences were for:

the signals of 6-H, 5-H, 7-H$_{syn}$, and the *tert*-butyl group in the case of **3**,

for those of 1-H, 7-H$_{syn}$, and 7-H$_{anti}$ in the case of **4**, and

for those of 6-H, 5-H, 1-H, and the *tert*-butyl group in the case of **5**.

Coalescence phenomena were also observed in each case in the ^{13}C NMR spectra of **3**−**5** at low temperatures. The ^{13}C NMR spectra of **3**−**5** at room temperature showed only one set of signals in each case (cf. Figure 7−9, Table 7−9). However, several signals were already broad and at −30 °C most of the signals were in each case either broadened or split into two, in ratios corresponding roughly to those observed in the ^{1}H NMR spectra. The splitting of the ^{13}C NMR signals was most extensive in the case of **5**. The spectrum of **3** at −40 °C showed two signals each for C(5), C(1), and the *C*Me$_3$ group, while that of **4** at −40 °C featured two signals each for the *C*Me$_3$ group, C(1), and C(6). The spectrum of **5** at −30 °C exhibited two signals each for C(3), C(9), C(6), C(5), C(7), C(4), and C(1), whereas a total of three signals appeared for C(2) and the *C*Me$_3$ group. Here, too, the differences in the chemical shifts for further species of **3**−**5** were in each case only small. The largest shift differences were found for:

the signals of C(5), C(1), and the *C*Me$_3$ group in the case of **3**,

those of the *C*Me$_3$ group, C(1), and C(6) in the case of **4**, and

the signals of C(3), C(9), C(6), C(5), and C(1) in the case of **5**.

In order to allow structural assignment of the two species of **3**−**5** observed in their ^{1}H NMR spectra at −30 °C to −50 °C, a ROESY[29] investigation was carried out. The absence of negative off-diagonal cross-peaks in the ROESY spectra of **3** at −80 °C (Figure 10) and of **5** at −60 °C (Figure 11) shows that the exchange between the two species of **3** and **5** at these temperatures is slow relative to the NMR timescale. The ROESY spectrum of **3** features, besides other cross-peaks, a cross-peak between the signals of the *tert*-butyl group and 6-H for the major species. No such

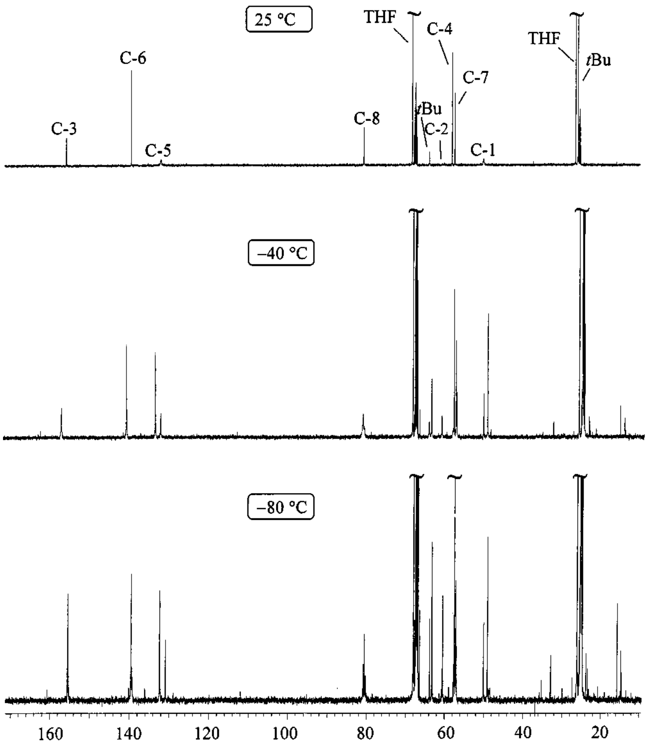


Figure 7. Temperature-dependent ^{13}C NMR spectra (125 MHz) of **3** in [D$_8$]THF.

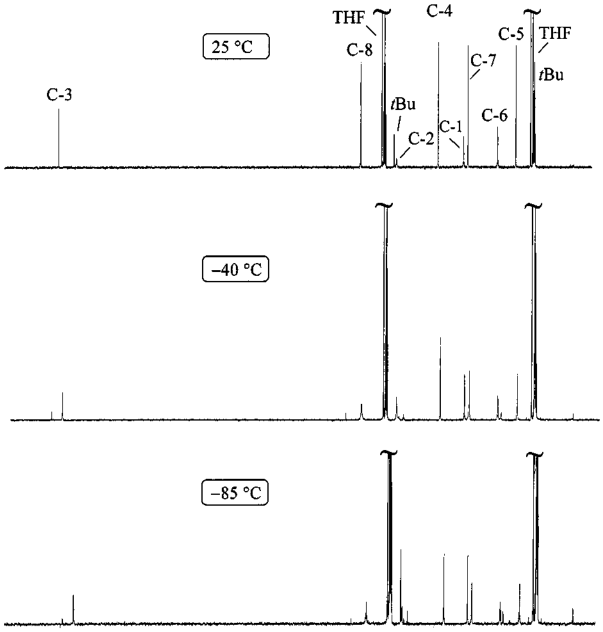


Figure 8. Temperature-dependent ^{13}C NMR spectra (125 MHz) of **4** in [D$_8$]THF.

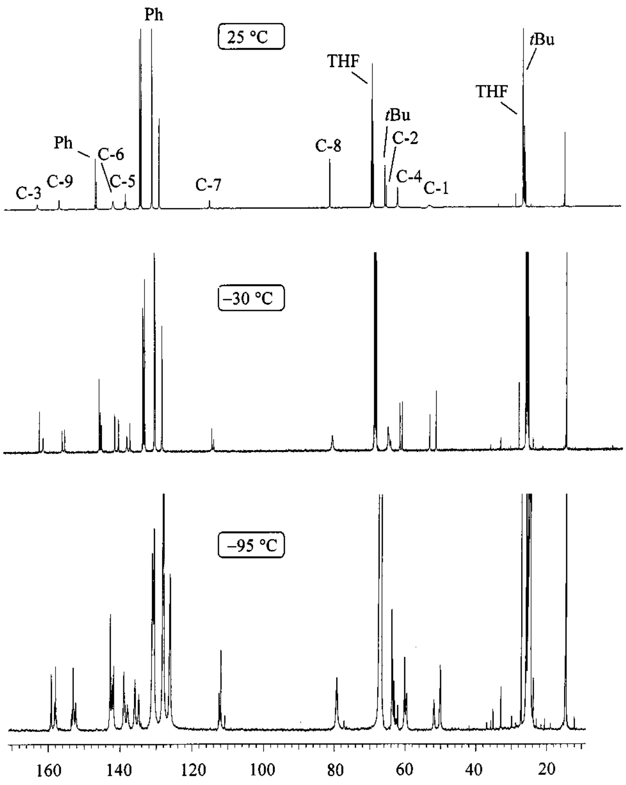
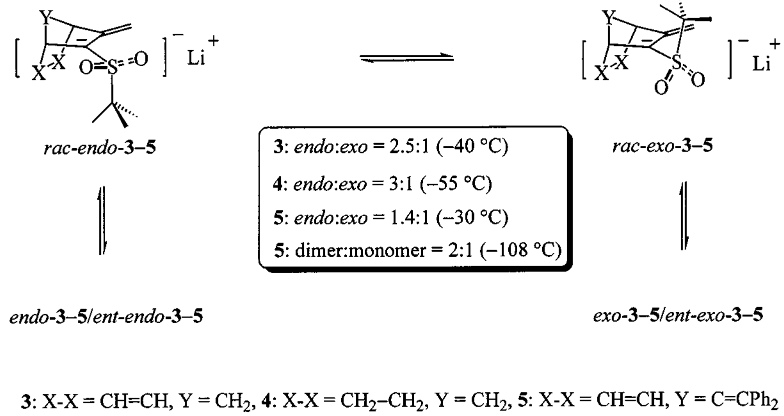


Figure 9. Temperature-dependent ^{13}C NMR spectra (125 MHz) of **5** in [D$_8$]THF.

cross-peak was observed for the minor species. Because of the small chemical shift differences for the *tert*-butyl group and 7-H$_{syn}$ of the minor species, observation of a cross-peak between those two signals was not possible. The ROESY spectrum of **5**, besides other cross-peaks, exhibited a cross-peak between the signals of the *tert*-butyl group and 6-H for the major species and two cross-peaks between the signal of the *tert*-butyl group and signals of the phenyl groups for the minor species. These results showed unequivocally that in the case of **3** and **5** the major species both have the *endo* Cα−S conformation and that the minor species both have the *exo* Cα−S conformation (vide infra). This assignment was corroborated by the opposite signs of the Δδ values (^{1}H NMR) for the signals of the *tert*-butyl groups of the minor and major species of **3** and **5**. While the *tert*-butyl signal of the minor species of **3** appeared at lower field than that of the major species, the signal of the minor species of **5** resonated at higher field than that of the major species. This opposite shift behavior can be connected with the effect of the ring current of the phenyl groups on the *tert*-butyl group in the *exo* conformer of **5**, which causes an upfield shift. A similar effect was observed in the case of the corresponding sulfones *exo*-**10** and *endo*-**10** (vide supra). Unfortunately, no similar structural assignment of the *endo* and *exo* diastereomers of **4** by ROESY experiments was possible, because of insufficient separation of key signals. We tentatively, however, also assign the *endo* conformation to the major species of **4** and the *exo* conformation to the minor species.

For the *endo*-*exo* diastereomerization of **3**, activation barriers of $\Delta G^{\#}_{270}$ = 13.1±0.1 kcal/mol and 12.6±0.1 kcal/mol were estimated at the coalescence temperature.[30] In the case of the *endo*-*exo* equilibration of **5**, the estimated activation barriers $\Delta G^{\#}_{288}$ at the coalescence temperature amounted to 13.5±0.1 kcal/mol and 13.3±0.1 kcal/mol.



Scheme 3. *Endo-exo* diastereomer and monomer-dimer equilibria of **3**−**5** in THF.

Table 5. ^{1}H NMR spectroscopic data (δ, ppm) of carbanion salts **3**−**5** in [D$_8$]THF at 25 °C.

Atom	3		4		5	
	δ	$\Delta\delta_1,\Delta\delta_2$ [a]	δ	$\Delta\delta_1,\Delta\delta_2$ [a]	δ	$\Delta\delta_1,\Delta\delta_2$ [a]
1-H	3.35	+0.05/+0.02	2.81	−0.01/−0.04	3.90	+0.11/+0.08
2-H	–	–	–	–	–	–
4-H	2.99	−0.40/−0.34	2.51	−0.36/−0.29	3.44	−0.52/−0.45
5-H$_{exo}$	5.93	−0.25/−0.36	1.55	−0.17/−0.17	6.21	−0.23/−0.31
5-H$_{endo}$	–	–	1.25	−0.15/−0.32	–	–
6-H$_{exo}$	6.22	−0.13/−0.07	1.66	+0.18/−0.06	6.57	+0.03/+0.05
6-H$_{endo}$	–	–	1.55	+0.25/−0.80	–	–
7-H$_{syn}$	1.52	−0.56/−0.03	1.46	−0.53/−0.02	–	–
7-H$_{anti}$	1.40	−0.29/−0.30	1.08	−0.26/−0.40	–	–
8-H$_{syn}$	3.95	−1.34/−1.33	3.67	−1.66/−1.76	4.03	−1.52/−1.31
8-H$_{anti}$	3.93	−1.46/−1.36	3.44	−1.78/−1.75	3.99	−1.48/−1.35

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

Table 6. ^{13}C NMR spectroscopic data (δ, ppm) of carbanion salts **3**−**5** in [D$_8$]THF at 25 °C.

Atom	3		4		5	
	δ	$\Delta\delta_1,\Delta\delta_2$ [a]	δ	$\Delta\delta_1,\Delta\delta_2$ [a]	δ	$\Delta\delta_1,\Delta\delta_2$ [a]
C(1)	49.8	+2.2/−1.6	45.3	+3.1/+3.8	51.8	+4.1/+2.7
C(2)	60.7	+0.7/−1.1	64.2	+1.1/+0.7	63.3	+0.4/+2.0
C(3)	155.7	+12.6/+11.5	158.4	+11.5/+12.3	159.2	+11.6/+10.4
C(4)	57.8	+8.2/+5.9	52.5	+8.3/+6.1	60.2	+7.3/+6.3
C(5)	131.8	−8.7/−3.5	30.7	+0.5/+2.2	135.0	−7.1/−0.7
C(6)	139.3	+4.6/+5.3	35.8	+8.4/+12.8	138.5	+4.7/+4.1
C(7)	57.1	+8.9/+7.3	44.8	+6.6/+4.4	112.1	−14.4/−11.6
C(8)	80.4	−32.1/−30.0	74.4	−37.3/−35.1	79.0	−33.3/−31.9
*C*Me$_3$	63.6	+2.6/+3.3	64.9	+4.1/+4.0	63.7	+2.3/+3.3
C*Me*$_3$	25.6	+1.5/+1.7	26.0	+1.8/+1.8	25.5	+1.2/+1.7

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

Table 7. ^{13}C NMR spectroscopic data (δ, ppm, 125 MHz) of carbanion salt **3** in [D$_8$]THF at different temperatures.

	25 °C	−40 °C	−80 °C
C(3)	155.06	155.51, 155.45	155.60, 155.53, 155.49, 155.40
C(6)	138.69	140.25, 139.45	139.59, 139.37, 139.28
C(5)	131.21	132.31, 131.00	132.37, 130.93
C(8)	79.81	80.85, 80.54, 80.20	80.85, 80.54, 80.20
*C*Me$_3$	63.13	63.28, 60.70	63.87, 63.30, 63.23
C(2)	60.00	60.70	60.62, 60.51, 60.45
C(4)	57.29	57.62	57.59, 57.53
C(7)	56.57	57.18, 57.06	57.19, 57.05
C(1)	49.25	50.23, 49.18	50.13, 49.06
C*Me*$_3$	25.08	25.42	26.19

Table 8. ^{13}C NMR spectroscopic data (δ, ppm, 125 MHz) of carbanion salt **4** in [D$_8$]THF at different temperatures.

	25 °C	−40 °C	−85 °C
C(3)	157.99	157.7 (br)	157.62, 157.47
C(8)	73.99	74.2 (br)	74.31, 74.07
*C*Me$_3$	64.55	64.3 (br)	64.26, 63.93, 63.79
C(2)	63.83	62.0 (br)	63.31, 62.32
C(4)	52.10	51.93	51.83, 51.73
C(1)	44.92	45.10, 43.80	44.98, 43.81
C(7)	43.76	43.70	43.73
C(6)	35.41	35.7 (br), 34.90	35.68, 35.55, 34.79
C(5)	30.31	30.1 (br)	32.91, 30.04
C*Me*$_3$	25.55	25.42	25.42, 25.16

These values correspond well to those estimated for the enantiomerization of the benzylic *tert*-butylsulfonyl carbanion salts **IIIa** ($\Delta G^{\#}_{283}$ = 13.5±0.2 kcal/mol) and **IIIb** ($\Delta G^{\#}_{295}$ = 14.2±0.3 kcal/mol) (Figure 12) at the respective coalescence temperatures in THF.[10] This comparison is based on the assumption that Cα−S bond rotation of the *endo* and *exo* diastereomers of **3** and **5** is, as with **IIIa** and **IIIb**, not only the rate-determining step but also a process mostly enthalpic in nature. The failure to observe the *endo* and the *exo* diastereomers of **1** and **2** by NMR spectroscopy at low temperatures, in the light of these results, finds its logical explanation in their significantly lower Cα−S rotational barriers compared to those in **3**−**5**. This is corroborated by the observation that the *S*-phenyl analogs of **IIIa** and **IIIb** have enantiomerization barriers of only approximately 10 kcal/mol at low temperatures.[10]

Carbanion salt **5**, according to cryoscopic results, forms monomers and dimers in THF solution. Hence, the two signal sets observed in the ^{1}H and ^{13}C NMR spectra of **5** at −30 °C must be averaged signal sets of those monomers and dimers with anions of *endo* conformation and of those monomers and dimers with anions of *exo* conformation. At

Table 9. ^{13}C NMR spectroscopic data (δ, ppm, 125 MHz) of carbanion salt **5** in [D_8]THF at different temperatures.

	25 °C	−30 °C	−95 °C
C(3)	159.0 (br)	159.35, 158.3 (br)	159.21, 159.06, 158.22, 158.00, 157.74
C(9)	153.0 (br)	153.18, 152.51	153.84, 153.13, 152.43
i-C	143.29, 142.89	143.13, 143.09, 142.76	142.85, 142.33, 141.90
C(6)	138.2 (br)	138.91, 137.90	139.1 (br), 138.1 (br)
C(5)	135.05	135.7 (br), 134.80	136.00, 134.97
o-C	131.23, 130.85	131.29, 131.20, 130.84	131.24, 130.77
m-C	127.92	128.14, 127.99, 127.92	128.19
p-C	125.95, 125.88	126.08, 125.99	126.29
C(7)	122.0 (br)	112.44, 111.93	112.53, 112.08, 110.93
C(8)	78.99	79.1 (br)	79.3 (br), 77.2 (br)
CMe_3	63.76	63.71 (br)	63.91, 63.72, 63.56, 63.28, 63.00
C(2)	63.32	63.04 (br)	62.21, 62.63, 62.51, 62.21
C(4)	60.25 (br)	60.41, 59.81	60.29, 59.68, 59.71
C(1)	41.6 (br)	52.17, 50.36	52.03, 50.24
C*Me*$_3$	25.48	25.67	26.19

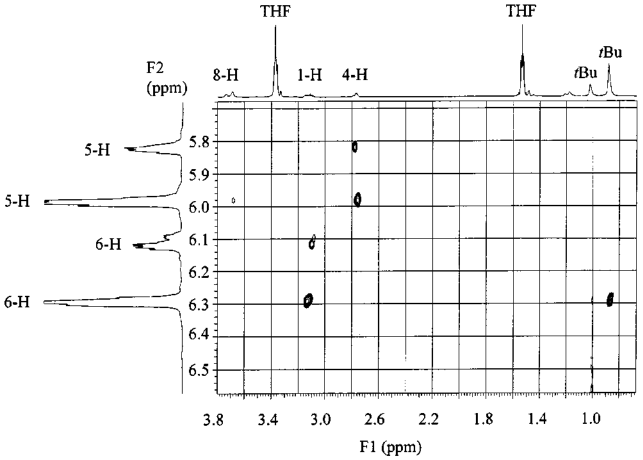


Figure 10. ROESY spectrum of **3** at −80 °C in [D_8]THF.

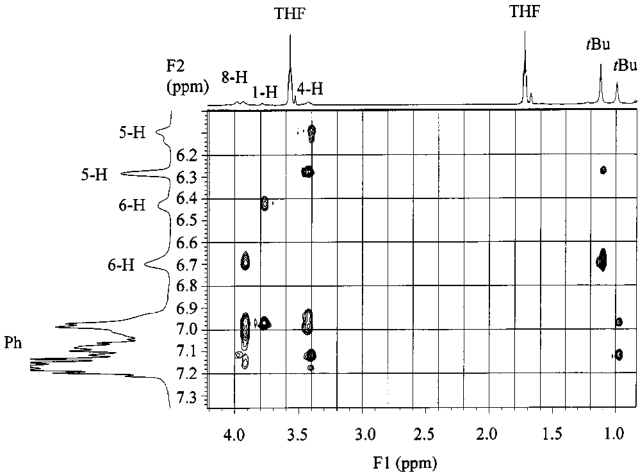
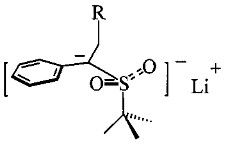


Figure 11. ROESY spectrum of **5** at −60 °C in [D_8]THF.



III

a: R = Ph, **b**: R = *t*Bu

Figure 12. Lithium salts of chiral benzylic α-sulfonyl carbanions.

this temperature, monomer-dimer equilibration is still fast on the NMR timescale. Thus, nothing can be said, on the basis of these results, of whether the monomers and dimers of **5** have the same or different conformational barriers. Carbanion salts **3** and **4** would be expected to behave similarly, and so the same arguments can be applied to their NMR spectra at −30 °C to −50 °C. It was now of considerable interest to see whether, upon lowering the temperature of the solutions of **3**−**5** even further, not only the *endo*-*exo* equilibrium but also the monomer-dimer equilibrium could be "frozen out" and thus all four species observed. Inspection of the ^1H NMR spectra of **3**−**5** at −30 °C to −50 °C found that several signals were already broad (*cf.* Figure 4−6). Upon cooling the solutions of the carbanion salts down to −100 °C, a second coalescence phenomenon was observed in each case, resulting in additional splitting of several signals. Differences in the chemical shifts of the signals of the additional species of **3**−**5** observed at −100 °C, however, were only small. The additional splitting at −95 °C was most pronounced in the case of the benzhydrylidene-substituted carbanion salt **5**. The signals of 6-H_{endo}, 6-H_{exo}, 5-H_{endo}, and 5-H_{exo} were each split into two, giving a total of eight signals, in integral ratios of approximately 6:1, 1:1, 10:1, and 2:1, respectively. The signal of 4-H was split into four. Because of signal overlap and line-broadening, these ratios are not very accurate, however. The ^{13}C NMR spectra of **3**−**5** at −100 °C also revealed a second coalescence phenomena in each case, and additional splitting of several signals, already broad at −30 °C to −50 °C, took place (cf. Figure 6−8, cf. Table 7−9). Here, too, the differences in the chemical shifts of corresponding ^{13}C NMR signals were only small. While the spectrum of **3** at −100 °C showed three signals each for C(3) and C(8), that of **4** exhibited three for C(6) and five signals for the *C*Me_3 group together with C(2). The additional splitting was again most pronounced in the case of **5**. The spectrum of **5** at −95 °C featured five signals for C(3), at least three for C(9), two broad signals for C(6), three for C(7), two broad signals for C(8), three signals for C(4), and a total of eight or perhaps nine signals for C(2) and the *C*Me$_3$ group.

The NMR spectroscopic data of **3**−**5** obtained at low temperatures can be interpreted as follows. The two sets of signals observed in the NMR spectra of **3**−**5** at −30 °C to −50 °C are averaged signals sets of *endo*-**3**−**5** monomers and of the corresponding *endo*-**3**−**5**/*ent*-*endo*-**3**−**5** dimers with anions of *endo* conformation, and of the *exo*-**3**−**5** monomers and the corresponding *exo*-**3**−**5**/*ent*-*exo*-**3**−**5** dimers with anions of *exo* conformation. The four sets of signals recorded at −90 °C to −100 °C thus belong to the four equilibrium species *endo*-**3**−**5**, *endo*-**3**−**5**/*ent*-*endo*-**3**−**5**, *exo*-**3**−**5**, and *exo*-**3**−**5**/*ent*-*exo*-**3**−**5** (Scheme 3). Thus, whereas the conformational exchange of carbanion salts **3**−**5** is already slow on the NMR timescale at −30 °C to −50 °C, exchange between aggregates is still fast. At −90 °C to −100 °C, however, both processes are slow on the NMR timescale. As mentioned above, the splitting of signals in the NMR spectra was most pronounced in the case of the carbanion salt **5**, which bears a benzhydrylidene group. Therefore, it might be argued that the additional splitting of signals in the NMR spectra of **5** at −90 °C to −100 °C is due to different conformers of the benzhydrylidene group rather than to monomers and dimers. However, from (i) the uniform behavior of **3**−**5**, (ii) the failure to observe a splitting of signals in the NMR spectra of sulfone *endo*-**10** at −90 °C (vide supra), and (iii) the low rotational barriers of 1,2-diphenylethenes in general,[20] we think that this argument is invalid (*cf.* Scheme 2) and that the signals observed correspond to the monomers, dimers, and diastereomers. The ^{1}H NMR spectrum of **5** at −95 °C features eight signals for 5-H and 6-H together. On the basis of the cryoscopically determined dimer-to-monomer ratio of **5** at −108 °C, approximately 2:1, we tentatively assign these signals to the monomers and dimers with anions of *exo* and *endo* conformation, as shown in Figure 6. This would suggest the conclusion that at this temperature the ratio of the *endo* and *exo* species is approximately 2:1 and that the ratio of the *endo* dimer and the *endo* monomer is larger (≈ 4:1) than the ratio of the *exo* dimer and the *exo* monomer (≈ 1:1). It should be noted, however, that this assignment has some uncertainties. Since the cryoscopic aggregation number and the integral ratios are fraught with relatively large errors, assignment of the signals for the *exo* monomers and the *exo* dimers in the spectrum of **5** is to some degree arbitrarily.

Additional support for the monomer-dimer and *endo*-*exo* equilibria of **5** was sought from a ^{6}Li NMR experiment. The ^{6}Li NMR spectrum of **5** in [D$_8$]THF at room temperature showed only one signal (Figure 13). At −50 °C, however, the signal became broad, and split into two signals in a ratio of approximately 1.9:1 at −98 °C. This ratio would correspond roughly to the dimer-monomer ratio determined by cryoscopy. The ^{6}Li NMR spectroscopic data could be interpreted by making the reasonable assumptions that at −98 °C the exchange of the Li atoms between monomers and dimers is slow relative to the NMR timescale and that the Li atoms of the *endo* and *exo* monomers on the one hand and those of the *endo* and *exo* dimers on the other hand are isochronous under the conditions employed.

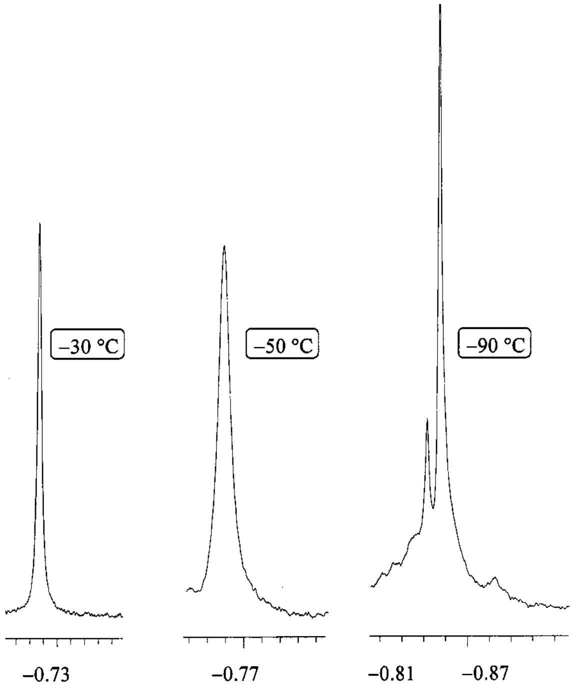
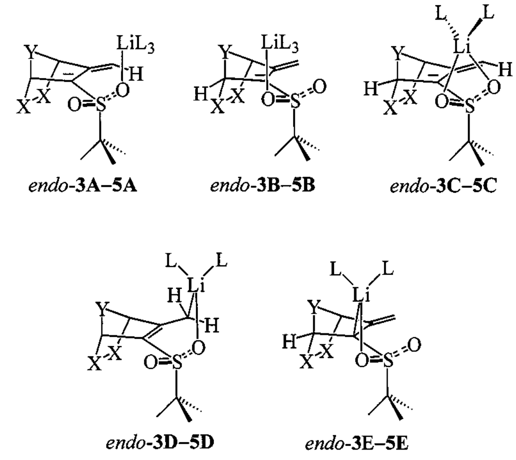


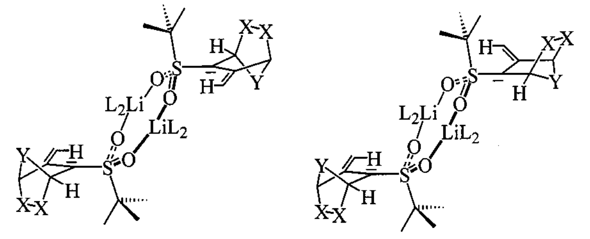
Figure 13. Temperature-dependent ^{6}Li NMR spectra (74 Hz) of **5** in [D$_8$]THF.

Experimental evidence having been obtained that **3**−**5** each exist in THF solution as a mixture of monomers and dimers, the anions of which adopt *endo* and the *exo* conformations, the question of their structures arises. Possible structures for the monomeric and dimeric CIPs of *endo*-



3: X-X = CH=CH, Y = CH$_2$
4: X-X = CH$_2$–CH$_2$, Y = CH$_2$
5: X-X = CH=CH, Y = C=CPh$_2$

Scheme 4. Possible structures of the monomers of **3**−**5** (L = THF).



endo-**3**–**5**/*ent*-*endo*-**3**–**5** *rac*-(*endo*-**3**–**5**)$_2$

3: X-X = CH=CH, Y = CH_2
4: X-X = CH_2–CH_2, Y = CH_2
5: X-X = CH=CH, Y = C=CPh_2

Scheme 5. Possible structures of dimers of **3**−**5** (L = THF).

3−**5** are depicted in Scheme 4 and Scheme 5, respectively. Those of *exo*-**3**−**5** should be similar and so are not shown in the Schemes. Whereas the Li atoms in the monomeric CIPs *endo*-**3A**−**5A** and *endo*-**3B**−**5B** and in the corresponding diastereomers *exo*-**3A**−**5A** and *exo*-**3B**−**5B** are each attached only to one O atom, those in the monomeric CIPs *endo*-**3C**−**5C** and their diastereomers *exo*-**3C**−**5C** are coordinated to both O atoms. A CIP structure of the type *exo*-**3A**−**5A** in the crystal is adopted by *exo*-**3**·PMDETA and by two further 12-crown-4 and PMDETA-coordinated lithium salts of α-sulfonyl carbanions,[12] while a CIP structure of type *endo*-**3C**−**5C** is adopted in the crystal by two 18-crown-6-coordinated potassium salts of α-sulfonyl carbanions.[23] In *endo*-**3D**−**5D** and *endo*-**3E**−**5E** and their diastereomers *exo*-**3D**−**5D** and *exo*-**3E**−**5E**, the Li atoms are coordinated both to the O atom and to either C(2) or C(8).

Probable structures for the dimers of *endo*-**3**−**5** and *exo*-**3**−**5** are *endo*-**3**−**5**/*ent*-*endo*-**3**−**5** (C_i) (Scheme 5) and *exo*-**3**−**5**/*ent*-*exo*-**3**−**5** (C_i) (not depicted in Scheme 5). CIP structures of the *endo*-**3**−**5**/*ent*-*endo*-**3**−**5** type are adopted in the crystal by the diglyme-solvated dimers *endo*-**1**−**2**/*ent*-*endo*-**1**−**2** (Figure 14). These dimers contain eight-membered rings composed of Li, O, and S atoms, typical of dimeric lithium salts of α-sulfonyl carbanions,[22] and each O atom carries a Li atom, which is not engaged in a bonding to the allylic moiety. In addition to these two dimers, the *tert*-butyl groups of which are *anti* with regard to the (Li−O−S−O)$_2$ ring, the two corresponding *syn* dimers (C_s) (not shown in Scheme 5) have to be considered. Furthermore, since **3**−**5** were studied as racemates, the homochiral *anti* dimers *rac*-(*endo*-**3**−**5**)$_2$ (C_2) and their *exo* isomers, as well as the two corresponding homochiral *syn* dimers (C_2) (not shown in Scheme 5), are further possible candidates. Finally, dimers composed of two anions with different Cα−S conformations can be imagined.

The monomers and dimers of *endo*-**3**−**5**, with anions of *endo* conformation, are the preferred equilibrium species. The reasons for the higher stability of the CPIs with *endo* conformations are not clear yet. Ab initio calculation of the counterion-free anions of **1** and **2** showed the *endo* diastereomers to be more stable than the *exo* diastereomers.[7]

In an attempt to shed some light on the modes of coordination of the Li atoms in the monomeric and dimeric CIPs of **3**−**5**, ^{6}Li,^{1}H HOESY experiments were performed on ^{6}Li-**5** in [D$_8$]THF. Salt **5** was chosen because the splitting of its signals was most pronounced in its low temperature NMR spectra. The HOESY spectrum of **5** at room temperature, at which the aggregational and conformational equilibria are fast on the NMR timescale, exhibits cross-peaks of equal intensity not only to 8-H_{syn} but also to 1-H and

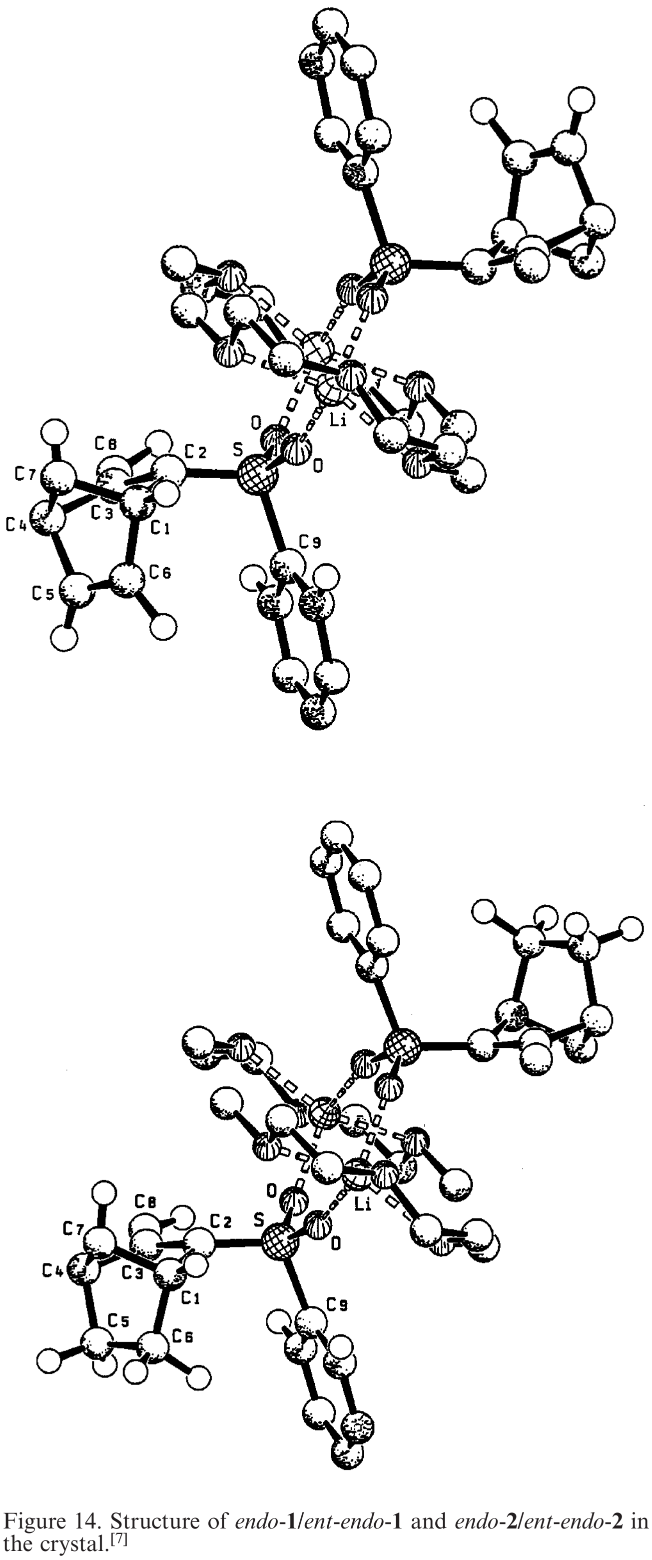


Figure 14. Structure of *endo*-**1**/*ent*-*endo*-**1** and *endo*-**2**/*ent*-*endo*-**2** in the crystal.[7]

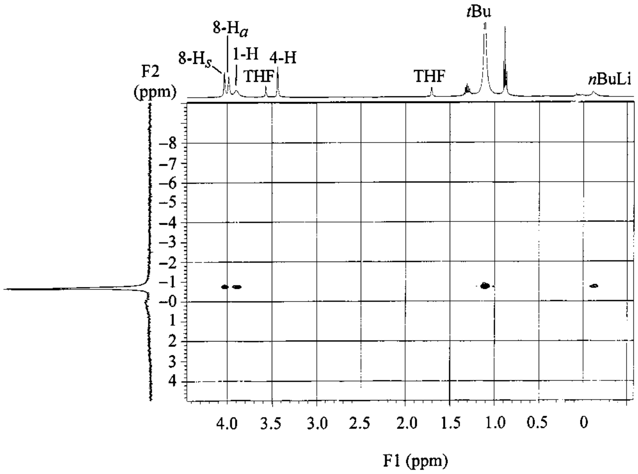


Figure 15. ^{6}Li,^{1}H-HOESY spectrum of **5** at 25 °C in [D$_8$]THF.

the *tert*-butyl group (Figure 15). Interestingly, the ^{6}Li,^{1}H HOESY spectra of **1** and **2** in THF solution at −75 °C, at which temperature there is still a fast equilibrium between the dimeric and monomeric CIPs (1:1), also exhibited equally intensive cross-peaks to 8-H$_{syn}$, H$_{ortho}$, and 1-H.[7] Such Li−H correlations would be compatible with a rapidly equilibrating mixture of the monomeric CIPs *endo*-**5A−E** and *exo*-**5A−E** and the dimeric CIPs *endo*-**5**/*ent*-*endo*-**5** and *exo*-**5**/*ent*-*exo*-**5**. The Li atoms in *endo*-**5A** and in *exo*-**5A** are spatially close to 8-H$_{syn}$, while those in *endo*-**5B** and *exo*-**5B** are close to 1-H. In the *exo*-**3**·PMDETA monomer, which may serve as a model for *exo*-**5A**, the Li−8-H$_{syn}$ distance is 326 pm. The monomers *endo*-**5C** and *exo*-**5C** should have Li−1-H and Li−8-H$_{syn}$ distances similar in length. In the dimers *endo*-**1**/*ent*-*endo*-**1**·2diglyme and *endo*-**2**/*ent*-*endo*-**2**·2diglyme, which can be taken as models for *endo*-**5**/*ent*-*endo*-**5** and *exo*-**5**/*ent*-*exo*-**5**, the shortest Li−8-H$_{syn}$, Li−1-H, and Li−H$_{ortho}$ distances are all in a range from 345 to 370 pm. Li−H distances of this sort, while being outside the bonding region, are, however, well within the limits of detection by ^{6}Li,^{1}H HOESY spectroscopy.[31] In contrast to *endo*-**5A−5C**, *exo*-**5A−5C**, *endo*-**5**/*ent*-*endo*-**5**, and *exo*-**5**/*ent*-*exo*-**5**, the monomers *endo*-**5D** and *endo*-**5E** and their *exo* diastereomers should be characterized by strong ^{6}Li,^{1}H correlations to 8-H$_{syn}$/8-H$_{anti}$ and 1-H, respectively, because of the presence of C−Li bonds. Because of the averaging of the Li−H correlations in the ^{6}Li,^{1}H NMR spectrum of **5** at room temperature, nothing can be said about which monomeric CIP is preferred. However, one would expect that, for both entropic and enthalpic reasons, monomers of type (**C**), (**D**), and (**E**), in which the anion coordinates the Li atom in a bidentate fashion, are favored in comparison to those with only one O−Li bond and which are solvated by three THF molecules. A recent ab initio study of the carbanion salt **Ia** ($R^1 = R^2 = H$, $R^3 = Ph$, L = THF, $n = 2$), the anion of which was fixed in the s-*cis* conformation, gave minimum energy CIP structures, all of which lay within 1 kcal/mol of each other and which featured either O,O-, O,Cα-, or O,Cγ-coordination of the Li atom.[9] Computational evidence was obtained that solvation of this salt by three THF molecules is energetically unfavorable. Because of the fast aggregational and conformational equilibria of **5** at room temperature, low temperature HOESY experiments were expected to be more fruitful. Much to our disappointment, however, ^{6}Li,^{1}H HOESY experiments on **5** at −100 °C were not successful because of insufficient peak separation of the 8-H and 1-H signals of the monomer and dimers.

Final points of structural interest were the coordination geometries of the allylic moieties in **3−5** in solution and the nature of the stabilization of the negative charge provided by the neighboring double bond. Inspection of Table 2 and Table 3 as well as Table 5 and Table 6 reveals the following shift variations (Δδ) in the NMR spectra on going from the sulfones **9**, **12**, and **10** to the carbanion salts **3−5**, respectively: (i) small variations in the C(2) signals, (ii) strong upfield shifts of the signals of C(8) and 8-H, and (iii) weaker, downfield shifts of the C(3) signals. Although these shift variations correspond in sign to those observed for **1** and **2**, the Δδ values for C(8) and 8-H of **3−5** are significantly larger in magnitude than those of their *S*-phenyl analogs (Table 10). It is generally accepted that two mutually antagonistic main effects contribute to the chemical shift variation of the ^{1}H and ^{13}C NMR signals on going from the carbon acid to the carbanion salt: an upfield shift due to the negative charge and a downfield shift in the case of a change of the coordination geometry from tetrahedral to planar.[32,33] The shift variations recorded for **3−5**[34] would thus be qualitatively compatible with allylic moieties featuring (i) more or less planar anionic C(2) atoms, (ii) accumulations of negative charge at C(2) and C(8), and (iii) accumulations of positive charge at C(3). This is corroborated in part by calculated charge densities for the allylic moieties of the counterion-free anions of **1** and **2**,[7] as well as of the CIPs of **Ia**.[9] The larger upfield shifts (Δδ) for C(8) and 8-H, as well as the almost constant position of the signals for C(2), in **3−5**, compared to **1** and **2**, point to larger accumulations of negative charge at C(8) in the former anions. In accordance with this interpretation is the observation that *exo*-**3**·PMDETA has an essentially planar anionic C(2) atom in the crystal, whereas the anionic C(2) atoms of *endo*-**1**/*ent*-*endo*-**1** and *endo*-**2**/*ent*-*endo*-**2** are significantly pyramidalized in the crystalline state (*cf.* Table 4) and most probably also in solution. Further confirmation for this notion may be seen in the observation that *endo*-**2**/*ent*-*endo*-**2** not only features an anionic C(2) atom less pyramidalized than that in *endo*-**1**/*ent*-*endo*-**1**, but also displays greater Δδ (8-H) and Δδ [C(8)) values than the latter dimer does (*cf.* Table 4).[7] Finally and most importantly, the almost identical chemical shifts of the signals for 8-H, C(2), C(3), and C(8) in *endo*-**3−5** and *exo*-**3−5** point to similar structures for the allylic moieties in the *endo* and *exo* diastereomers. The two mechanisms resulting in charge distributions of the type $C(2)^-{-}C(3)^+{-}C(8)^-$ in **3−5** are allylic delocalization and/or polarization of the C(3)−C(8) double bonds by the negative charges at C(2). Since the degrees of accumulation of negative charge at C(8) in **3−5** by allylic delocalization, but not by polarization, depend on the coordination geo-

Table 10. ^{1}H and ^{13}C chemical shift variations (Δδ) upon formation of carbanion salts **1−5** from the corresponding sulfones

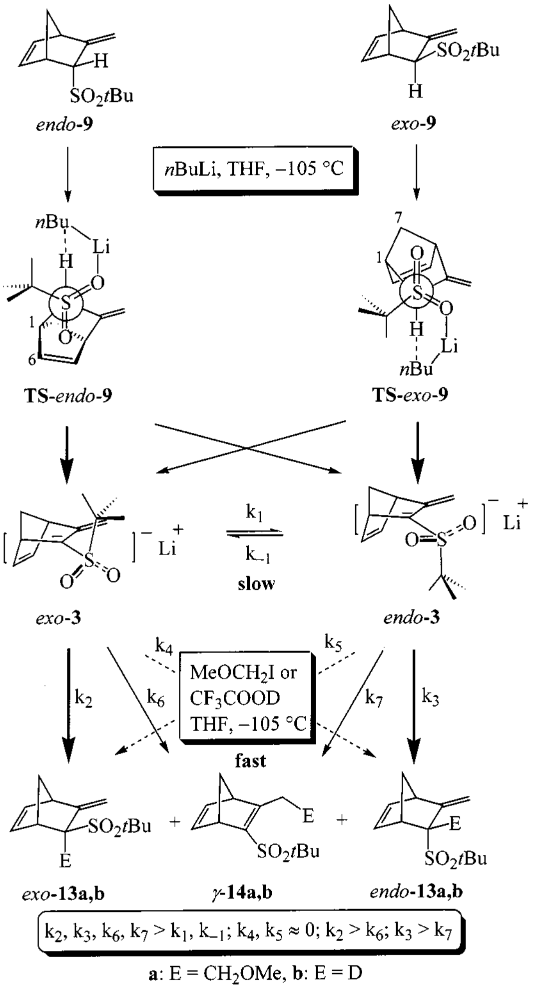
[a]	**1**	**2**	**3**	**4**	**5**
Δδ (8-H$_{syn}$)	−0.87/−1.08	−1.14/−1.17	−1.34/−1.33	−1.66/−1.76	−1.52/−1.31
Δδ (8-H$_{anti}$)	−1.13/−1.11	−1.49/−1.44	−1.46/−1.36	−1.78/−1.76	−1.48/−1.35
Δδ [C(8)]	−27.3/−26.1	−32.7/−31.1	−32.1/−30.0	−37.3/−35.1	−33.3/−31.9

[a] The first value refers to $\delta_{\text{lithiosulfone}} - \delta_{exo\text{ sulfone}}$ and the second value to $\delta_{\text{lithiosulfone}} - \delta_{endo\text{ sulfone}}$.

metries of the allylic moieties, the NMR spectroscopic data support the notion[7] that allylic delocalization and not polarization of negative charge, together with the effects exerted by the sulfonyl group, in **3−5** are the dominating stabilizing factors in **3−5**.

3. Reactions between the Lithium Salts of the Allylic *S-tert*-Butylsulfonyl Carbanions and Electrophiles

Because of the relatively high *endo-exo* diastereomerization barriers of *endo*-**3−5** and *exo*-**3−5**, the chances for kinetic quenching (k_2, k_3 >> k_1, k_{-1}) of the diastereomers with reactive electrophiles, and thus for determination of their stereoselectivities, seemed to be good. The stereoselectivity studies of **3−5** described below were carried out in the knowledge of the principle limitation to which they were subject. The structural studies of **3−5** discussed above had revealed the existence of diastereomers, monomers, and dimers. Furthermore, the monomers and dimers most probably adopt different CIP structures. All these species might in principle exhibit not only different stereoselectivities but also different regioselectivities. Firstly, however, the observed selectivities would be only averages of the individual selectivities, the contributions of which might be difficult to discern. Secondly, the *endo-exo* isomerization barriers of the *endo* and the *exo* diastereomers are different. This would result in faster isomerization of the *exo* diastereomers, and thus to changes in the initial ratios of the diastereomers formed in the deprotonation step. Thirdly, interpretation of the selectivities would have to be based on the assumption of kinetics approaching either kinetic quenching or the C−H limit, which themselves are approximations. Fourthly, in a reaction with a given electrophile there could be competition between inter- and intramolecular pathways, which may have different selectivities. Finally, formation of the *endo* and *exo* diastereomers as well as their kinetic quenching would be accompanied to a certain extent by *endo-exo* isomerization because of their half-lives, which are only in the range of hours at −105 °C.



Scheme 6. Synthesis and reactivity of *endo*-**3** and *exo*-**3**. For clarity, *n*BuLi is depicted as a monomer in the structural representation of the transition state of deprotonation, although it is not known whether it is the monomer, dimer, or tetramer that reacts.

Deuteration experiments proved that deprotonation of *endo*-**9** and *exo*-**9** with *n*BuLi at −100 °C was fast and complete within a short time (Scheme 6). As a reactive alkylating reagent, the iodide MeOCH$_2$I was chosen. Reactions between *endo*-**3** and *exo*-**3** and this iodide at −105 °C were complete within five minutes. Treatment of *endo*-**9** with *n*BuLi at −105 °C in THF, followed after half a minute had elapsed (since completion of the addition of the base; termed as *endo-exo* isomerization time, t_{isn}) by addition of ten equivalents of MeOCH$_2$I at −105 °C, quantitatively gave a mixture of the sulfones *endo*-**13a**, *exo*-**13a**, and γ-**14a** in a ratio of 5:82:13, the major isomer being the *exo* sulfone (Table 11, entry 2). At t_{isn} = 0.25 min, conversion of the carbanion salts was not yet complete (Table 11, entry 1). With increasing t_{isn}, the *endo*-**13a**/*exo*-**13a**/γ-**14a** ratio changed from mainly *exo* sulfone to mainly *endo* sulfone and converged after t_{isn} = 30 min to a ratio of 43:30:27 (Table 11, entry 5). Interestingly, the amount of the γ-alkylated sulfone γ-**14a** also increased with increasing t_{iso}. In a final experiment, the solution of the carbanion salt was kept for two hours at room temperature in order to ensure complete *endo-exo* isomerization before addition of the iodide at −105 °C. In this case, the sulfones *endo*-**13a**, *exo*-**13a**, and γ-**14a** were isolated in a ratio of 44:22:34 (Table 11,

Table 11. Treatment of carbanion salt **3** with $MeOCH_2I$ at −105 °C in THF with formation of sulfones *endo*-**13a**, *exo*-**13a**, and γ-**14a**.

Entry	Starting material **9**	t_{isn} (min)	Products *endo*:*exo*:γ[a]	Yield (%)
1	*endo*	0.25	0:87:13[b]	–
2	*endo*	0.5	5:82:13	≥ 98
3	*endo*	5	13:72:15	≥ 98
4	*endo*	6	16:67:17	≥ 98
5	*endo*	30	43:30:27	≥ 98
6	*endo*	120[c]	44:22:34	≥ 98
7	*exo*	0.25	56:6:38[d]	–
8	*exo*	0.5	59:9:32[e]	–
9	*exo*	5	59:14:27	≥ 98
10	*exo*	6	55:14:31	≥ 98
11	*exo*	30	50:22:28	≥ 98
12	*exo*	120[c]	43:22:35	≥ 98

[a] According to GC. – [b] 55% of *endo*-**9** were recovered. – [c] The solution was allowed to warm to room temperature and quenched at −105 °C. – [d] 75% of *exo*-**9** were recovered. – [e] 37% of *exo*-**9** were recovered.

entry 6). A similar series of experiments was carried out starting with the *exo* sulfone *exo*-**9**. Treatment of *exo*-**9** with *n*BuLi at −105 °C, followed by addition of the iodide at −105 °C after t_{isn} = 5 min, gave the sulfones *endo*-**13a**, *exo*-**13a**, and γ-**14a** in a ratio of 59:14:27, the major isomer now being the *endo* sulfone (Table 11, entry 9). Noteworthy was the formation of a larger quantity of the γ-alkylation product in the case of the *exo* sulfone as starting material. A gradual increase of t_{isn} saw only small changes of the product ratio (Table 11, entries 10 and 11). In the final experiment, the solution of the carbanion salt was kept for two hours at room temperature in order to ensure complete *endo*-*exo* isomerization before addition of the iodide at −105 °C. In this case, the sulfones *endo*-**13a**, *exo*-**13a**, and γ-**14a** were isolated in a ratio of 43:22:35 (Table 11, entry 12). Thus, starting either from *endo*-**9** or from *exo*-**9** and allowing for complete *endo*-*exo* isomerization of **3** before addition of the iodide gave the alkylated sulfones in almost the same ratios. The configurations of *endo*-**13a** and *exo*-**13a** were determined by NOE experiments and on the basis of characteristic chemical shift differences in their NMR spectra, taking those of *endo*-**9** and *exo*-**9** as references.

The variation of the regio- and stereoselectivities of the methoxymethylation of *endo*-**3** and *exo*-**3** with increasing t_{isn} can be taken as an indication that the reaction with the electrophile and *endo*-*exo* isomerization approach kinetic quenching at −105 °C. Table 11 shows that the deprotonation-quenching sequence starting with the *endo* sulfone *endo*-**9** gives the *exo* sulfone *exo*-**13a** with high selectively, while that of the *exo* sulfone *exo*-**9** highly selectively affords the *endo* sulfone *endo*-**13a**. This interpretation of the observed ratios of the sulfones seems at first glance to be obscured by the relatively large amounts of the γ-substituted sulfone γ-**18a** formed. The apparent uncertainty disappears, however, on comparison of the regioselectivities obtained after a short t_{isn} and after the establishment of the approximately 3:1 equilibrium ratio of *endo*-**3** and *exo*-**3** at −105 °C (*cf.* Table 11, entries 1, 6, 7, and 12), which reveals that the α,γ-selectivities of *exo*-**3** and *endo*-**3** are different and amount roughly to 87:13 and 56:38, respectively. How can these selectivities be explained? While the difference in α,γ-selectivity is discussed in the context of the methylation of these salts (vide infra), interpretation of the stereoselectivities is attempted as follows. It was observed previously that the chiral, nonracemic benzylic α-sulfonyl carbanion salts **IIIa** and **IIIb**, which also have planar anionic C atoms, and other chiral α-sulfonyl carbanion salts react with electrophiles at the anionic C atom with very high selectivities from the side *syn* to the O atoms.[10] We therefore postulate that *endo*-**3** and *exo*-**3** behave in a similar manner. Thus, the selective formation of *exo*-**13a** and *endo*-**13a** from *endo*-**9** and *exo*-**9**, respectively, could be explained by assuming that (i) the deprotonation of *endo*-**9** and *exo*-**9** with *n*BuLi at −105 °C in THF highly selectively gives *exo*-**3** and *endo*-**3**, respectively, (ii) *exo*-**3** reacts with the electrophile at the anionic C(2) atom with high selectivity from the *endo* side to furnish *exo*-**13a** ($k_2 >> k_4$), while *endo*-**3** reacts with equally high selectivity from the *exo* side to yield *endo*-**13a** ($k_3 >> k_5$), and (iii) the asymmetric induction provided by the bicyclic ring system is negligible compared to that provided by the sulfonyl group. The proposed selective deprotonation of *endo*-**9** and *exo*-**9** with formation of *exo*-**3** and *endo*-**3**, respectively, could be explained by assumption of (i) an intramolecular deprotonation following coordination of *n*BuLi by the sulfone in a monodentate fashion, (ii) the attainment of the transition states (TSs) **TS**-*endo*-**9** and **TS**-*exo*-**9**, in which the *tert*-butyl group occupies the sterically least encumbered position, this being that gauche to 1-H and approximately *anti* to C(3), and (iii) a preferential clockwise rotation of the sulfonyl group around the C(2)−S bond in **TS**-*endo*-**9** and a counterclockwise rotation around this bond in **TS**-*exo*-**9**, together with planarization of C(2) following proton transfer to give *exo*-**3** and *endo*-**3**, respectively. Although the timing of planarization and rotation on the way from **TS**-*endo*-**9** to *exo*-**3** and from **TS**-*exo*-**9** to *endo*-**3** is not known, a C(2)−S bond rotation in the opposite direction with formation of the respective opposite diastereomeric anion should be less preferred because of severe torsional interactions resulting otherwise, mainly between the *tert*-butyl group and the C(2)−C(1) bond as well as C(1). If, in the deprotonation transition states, *n*BuLi were coordinated by both O atoms of the sulfonyl group of *endo*-**9** and *exo*-**9** in bidentate fashion, then the opposite prediction concerning the selectivity would have to be made: i.e., *endo*-**9** would give *endo*-**3** and *exo*-**9** would yield *exo*-**3**. However, these transition states, in which the 2-H atom would approximately bisect the O−S−O angle, should be much higher in energy because of the resulting steric interactions between the *exo tert*-butyl group and C(1)/C(7) and between the *endo tert*-butyl group and C(1)/C(6). Support for the above assumption of selective deprotonation of the *endo* and *exo* sulfones is provided by the deprotonation of enantiomerically pure acyclic *tert*-butyl sulfones with lithium organyls in THF at low temperatures, which proceeds with high enantioselectivity.[10d,10e]

Since NMR spectroscopy on **3** had demonstrated the existence of a fast equilibrium between monomers and dimers, the question arises of which species is the reactive one. A definite answer cannot be given at present. However, inspection of the crystal structures of the dimers *endo*-**1**/*ent*-*endo*-**1** and *endo*-**2**/*ent*-*endo*-**2**[7] and that of the monomer *exo*-**3**·PMDETA, which may serve as models for the monomers and dimers of **3** in solution, reveals pronounced shielding of the C(2) atoms of the dimers by the diglyme molecules and by parts of the respective other anion and a much less shielded C(2) atom in the monomer. Thus, it seems likely that the monomers of **3** are more reactive than the dimers. In the case of the reaction of the monomer (**C**), one has to postulate prior dissociation of a THF molecule to give a species with a tricoordinate Li atom, because of the otherwise resulting steric shielding of the C(2) atom by the THF molecule in the *syn* position.

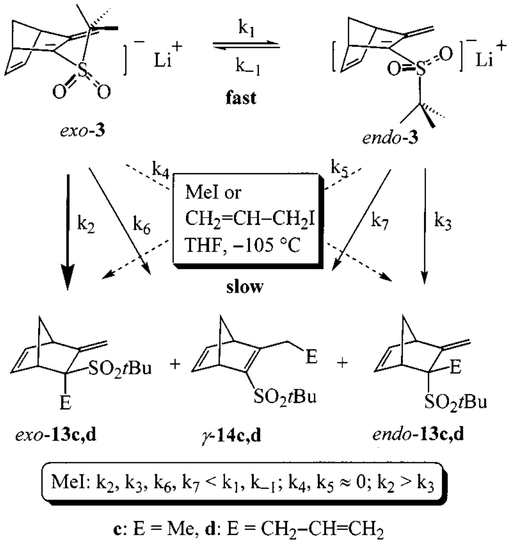
Next, the deuteration of *endo*-**3** and *exo*-**3** with CF_3COOD at low temperatures was studied. Treatment of *endo*-**9** with *n*BuLi at −105 °C, followed by addition of ten equivalents of CF_3COOD at −105 °C after t_{isn} = 15 s, afforded a mixture in which the *endo* sulfone *endo*-**13b** dominated (Table 12, entry 1). A gradual increase in t_{isn} saw a change of the ratio of the deuterated sulfones from mainly *exo* sulfone to mainly *endo* sulfone, which finally converged at t_{isn} = 2.5 h (−105 °C) to a ratio of 59:29:12 (Table 12, entries 2−7). When the solution of the carbanion salt was kept for two hours at room temperature and then quenched at −105 °C, the sulfones *endo*-**13b**, *exo*-**13b**, and γ-**14b** were isolated in a ratio of 67:22:11 (Table 12, entry 8). A similar series of deprotonation/deuteration experiments involving *exo*-**9**, *n*BuLi, and CF_3COOD at −105 °C with variation of t_{isn}, while keeping the solution of the carbanion salt at −105 °C, in all cases gave mixtures in which the *endo* sulfone *endo*-**13b** dominated (Table 12, entries 10−16). Here, too, the solution of the carbanion salt was kept for two hours at room temperature in a final experiment, before quenching at −105 °C. This furnished a mixture of the sulfones *endo*-**13b**, *exo*-**13b**, and γ-**14b**, in a ratio of 70:23:7 (Table 12, entry 17). Finally, treatment of *endo*-**9** and *exo*-**9** with *n*BuLi at −78 °C in THF, followed by addition of CF_3COOD at −78 °C after the solution of the carbanion salt had been kept for thirty minutes at −78 °C, gave a mixture of *endo*-**13b**, *exo*-**13b**, and γ-**14b** in both cases, and in the same ratio of 60:34:6 (Table 12, entries 9 and 18). The results obtained in the deprotonation of the sulfones and in the deuteration of *endo*-**3** and *exo*-**3** at −105 ° C roughly parallel those recorded in the methoxymethylation and indicate kinetic quenching.[35] There are, however, significant differences in the regio- and stereoselectivities compared to those of methoxymethylation. The differences between alkylation and deuteration may at least in part be associated with the different nature of the electrophiles $MeOCH_2I$ and CF_3COOD. In the latter case, the carbanion salts are most probably treated in reality with a mixture of electrophiles containing D atoms, such as, for example, the monomeric acid, its acid-base complex with THF, and the dimeric acid, all of which could exhibit different stereo- and regioselectivities. In addition, the existence of two different reaction paths, an inter- and intramolecular deuteration, which might also exhibit different regio- and stereoselectivities, cannot be ruled out.

Table 12. Treatment of carbanion salt **3** with CF_3COOD in THF with formation of sulfones *endo*-**13b**, *exo*-**13b**, and γ-**14b**.

Entry	Starting material **9**	T (°C)[a]	t_{isn} (min)	Products *endo*:*exo*:γ[b]	Yield (%)
1	*endo*	−105	0.25	11: 63:26	92
2	*endo*	−105	5	25: 57:18	92
3	*endo*	−105	10	29:56:15	94
4	*endo*	−105	15	37:47:16	92
5	*endo*	−105	45	49:35:16	96
6	*endo*	−105	90	52:32:16	96
7	*endo*	−105	150	59:29:12	98
8	*endo*	−105	120[c]	67:22:11	99
9	*endo*	−78	30	60:34:6	96
10	*exo*	−105	0.25	62:26:12[d]	78
11	*exo*	−105	1	53:35:12	98
12	*exo*	−105	3	54:31:15	99
13	*exo*	−105	5	62:26:12	96
14	*exo*	−105	10	55:34:11	99
15	*exo*	−105	15	59:31:10	92
16	*exo*	−105	30	48:40: 12	98
17	*exo*	−105	120[c]	70:23:7	86
18	*exo*	−78	30	60:34:6	84

[a] Deprotonation and reaction temperature. − [b] According to GC. − [c] The solution was allowed to warm to room temperature and quenched at −105 °C. − [d] 14% of *exo*-**9** were recovered.

Finally, the alkylations of *endo*-**3** and *exo*-**3** with MeI and allyl iodide were investigated, in anticipation that alkylation and *endo*-*exo* isomerization in these cases would approach the C-H limit (Scheme 7).



Scheme 7. Alkylation of *endo*-**3** and *exo*-**3**.

As shown in entries 1−14 in Table 13, treatment of *endo*-**9** and *exo*-**9** with *n*BuLi at −78 °C and −105 °C, followed by addition of ten equivalents of MeI at −78 °C or −105

Table 13. Treatment of carbanion salt **3** with MeI in THF with formation of sulfones *endo*-**13c**, *exo*-**13c**, and γ-**14c**.

Entry	Starting material **9**	*T* (°C)[a]	t_{isn} (min)	t_{ren} (min)	Conversion (%)	Products *endo*:*exo*:γ[b]	Yield (%)[c]
1	*endo*	−105	5	5	23	17:83:0	90
2	*endo*	−105	5	45	82	20:78:2	99
3	*endo*	−105	5	120	100	24:74:2	99
4	*endo*	−105	in situ[d]	120	100	18:80:2	98
5	*endo*	−105	120[e]	120	100	34:66:0	90
6	*endo*	−78	30	120	100	29:64:7	98
7	*endo*	−78	in situ[d]	120	100	26:67:7	89
8	*exo*	−105	5	5	14	36:64:0	92
9	*exo*	−105	5	45	67	32:65:3	98
10	*exo*	−105	5	120	100	32:66:2	90
11	*exo*	−105	in situ[d]	120	7	34:66:0[g]	–
12	*exo*	−105	120[e]	120	100	34:66:0	99
13	*exo*	−78	30	120	100	29:64:7	90
14	*exo*	−78	in situ[d]	120	22	29:64:7[f]	93

[a] Deprotonation and reaction temperature. − [b] According to GC. − [c] Based on conversion. − [d] A mixture of the carbon acid and methyl iodide was treated with *n*BuLi.− [e] The solution was allowed to warm to room temperature and quenched at −105 °C. − [f] 68% of *exo*-**9** were recovered. − [g] 82% of *exo*-**9** were recovered.

Table 14. Treatment of carbanion salt **3** with allyl iodide at −105 °C in THF with formation of sulfones *endo*-**13d**, *exo*-**13d**, and γ-**14d**.

Entry	Starting material **9**	t_{isn} (min)	t_{ren} (min)	Conversion (%)	Products *endo*:*exo*:γ[a]	Yield (%)[b]
1	*endo*	1	10	18	2:11:87	95
2	*endo*	1	60	49	6:27:67	98
3	*endo*	1	120	68	12:37:51	99
4	*endo*	120[c]	120	65	9:25:66	99
5	*exo*	1	10	20	2.5:7.5:90	91
6	*exo*	1	60	41	5:27:68	98
7	*exo*	1	120	56	11:32:57	98
8	*exo*	120[c]	120	55	10:29:61	88

[a] According to GC. − [b] Based on conversion. − [c] The solution was allowed to warm to room temperature and quenched at −105 °C.

°C after various t_{isn} values, after a certain reaction time (t_{ren}), invariably gave mixtures of *endo*-**13c**, *exo*-**13c**, and γ-**14c** in which the *exo* sulfone dominated to a similar extent. Methylation was much slower than methoxymethylation, as shown by the time required for complete conversion of the carbanion salt at low temperatures. These results show that methylation and isomerization of *exo*-**3** and *endo*-**3** approach the C−H limit, as in the case of **1** and **2**. This is corroborated by the results of reactions in situ (Table 13, entries 4, 7, 11, and 14). Thus, the selectivity of the methylation of *endo*-**3** and *exo*-**3** is determined primarily by the difference in the rate at which *exo*-**3** reacts from the *endo* side and *endo*-**3** from the *exo* side at the C(2) atom. This suggests the conclusion that attack of MeI at C(2) of *exo*-**3** from the *endo* side, giving the *exo* sulfone, must be faster than attack of the iodide at C(2) of *endo*-**3** from the *exo* side, yielding the *endo* sulfone: i.e., $k_2 > k_3$. In the case of the methylation of *endo*-**1** and *exo*-**1**, however, the *endo* diastereomer reacted faster than that the *exo* diastereomer: i.e., $k_3 > k_2$. How can the opposing reactivities of the diastereomers of the *S*-phenyl- and the *S*-*tert*-butyl-substituted carbanion salts be explained? The carbanion salts **3** and **1** differ structurally in two important aspects. Whereas **3** carries the bulky *tert*-butyl group at the S atom, salt **1** bears the less bulky phenyl group. Secondly, while C(2) in *endo*-**3** is planar, that in *endo*-**1** is strongly pyramidalized. The same difference with regard to the coordination geometry of C(2) should exist between *exo*-**3** and *exo*-**1**. It is assumed that in the TSs of *endo* methylation of *exo*-**3**, which gives the *exo* sulfone, and of *exo* methylation *endo*-**3**, which yields the *endo* sulfone, partial $sp^2 \rightarrow sp^3$ rehybridization of C(2) and partial rotation around the C(2)−S bond occur. The S−C(2)−C(1)−C(7) torsional angle in sulfone *exo*-**13c** is larger than the S−C(2)−C(1)−C(6) torsional angle in *endo*-**13c**. This difference should already be expressed to some extent in the corresponding TSs with regard to the C(2)−S bond. As a consequence, the developing eclipsing of the C(2)−S and the C(1)−C(7) bonds in the *endo* TS should be less than that of the C(2)−S bond and the C(1)−C(6) bond in the *exo* TS. In addition, the developing steric interaction between the *tert*-butyl group and C(6) in the *exo* TS would be expected to be greater than that between the *tert*-butyl group and C(7) in the *endo* TS. As a consequence, the *endo* TS should be lower in energy and hence the *exo* sulfone should be formed preferentially. Of crucial importance to this model are the extents of rehybridization of C(2) and of the C(2)−S bond rotation in the TSs. Unfortunately, both are unknown at present. In summary, this selectivity model for the methylation of *endo*-**3** and *exo*-**3** considers the difference in intramolecular interactions in the *endo* and *exo* TS to be decisive. In contrast, the selectivity model for *endo*-**1** and *exo*-**1** regards the difference in intermolecular interactions in the *endo* and *exo* TSs as decisive.[7] The C(2) atoms in *endo*-**1** and in *exo*-**1**, which carry the less bulky phenylsulfonyl group, are already strongly pyramidalized in the ground state.[7] Because of this and because of the smaller size of the phenyl group, intramolecular interactions in the TSs of methylation of *endo*-**1** and *exo*-**1** of the aforementioned type should be less important and intermolecular interactions should dominate. Eclipsing of the developing C(2)−Me bond and the C(1)−C(7) bond in the TS of α-*exo* methylation of *endo*-**1** [*exo* pyramidalization of C(2)] is less than that of the developing C(2)−Me and the C(1)−C(6) bonds in the TS of α-*endo* methylation of *exo*-**1** (*endo* pyramidalization of C(2)]. Hence, *endo*-**1** should react faster from the *exo* side than *endo*-**1** from the *exo* side.[7] In this context, a discussion of the different regioselectivities of *endo*-**3** and of *exo*-**3** recorded in their alkylation with $MeOCH_2I$ under kinetic quenching conditions seems appropriate. From an inspection of Table 11, it follows that the *endo* diastereomer possesses an α,γ-selectivity towards this electrophile significantly lower than that of the *exo* diastereomer. In other words, *endo*-**3** reacts at the α-position to a lesser extent than *exo*-**3**. The arguments applied to the TSs of methylation of *endo*-**3** and *exo*-**3** should also be applicable to the TSs of methoxymethylation. Thus, γ-attack of *endo*-**3** occurs to a greater extent than in the case of *exo*-**3** because of the higher energy of the α-*exo* TS of *endo*-**3**. The reaction of *endo*-**3** and *exo*-**3** with ten equivalents of allyl iodide at −105 °C in THF, which gave a mixture of *endo*-**13d**, *exo*-**13d**, and γ-**14d**, took a similar course to that with MeI, except that it was much slower and occurred preferentially at the γ-position (Table 14, entries 1−8). This shows that allylation of *exo*-**3** and *endo*-**3** also approaches the C−H limit. Diastereomer *exo*-**3** reacts more rapidly than diastereomer *endo*-**3** at the α-position. Interpretation of the stereoselectivities, however, is hampered by the low α,γ-regioselectivity, discussed later. The significantly lower α,γ-selectivity of the allylation of *endo*-**3** and *exo*-**3** compared to their methylation at the C−H limit may be explained by the greater steric size of allyl iodide compared to MeI.

The configurations of *endo*-**13c** and *endo*-**13d**, and of *exo*-**13c** and *exo*-**13d**, were assigned on the basis of NOE experiments and the observation of similar chemical shift differences in their NMR spectra, as found in the case of *endo*-**9** and *exo*-**9**. Sulfone *exo*-**13c** was obtained in a diastereomerically pure state by chromatography and its NMR signals were fully assigned by two-dimensional methods and NOE experiments. The final proof for the configuration of *exo*-**13c** was provided by an X-ray crystal structure analysis (Figure 16).[18] The positions of the sulfonyl and methyl group are characterized by the torsion angles C(10)−C(2)−C(1)−C(6) and S−C(2)−C(1)−C(7), the values of which are 53.2° and 76.1°, respectively.

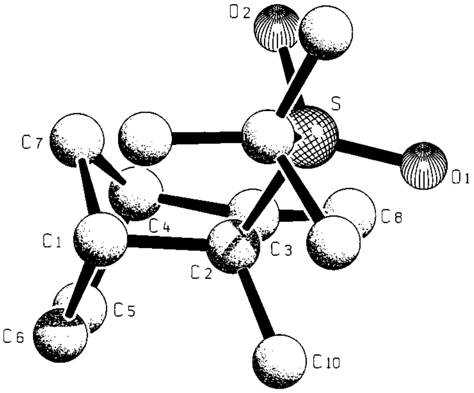
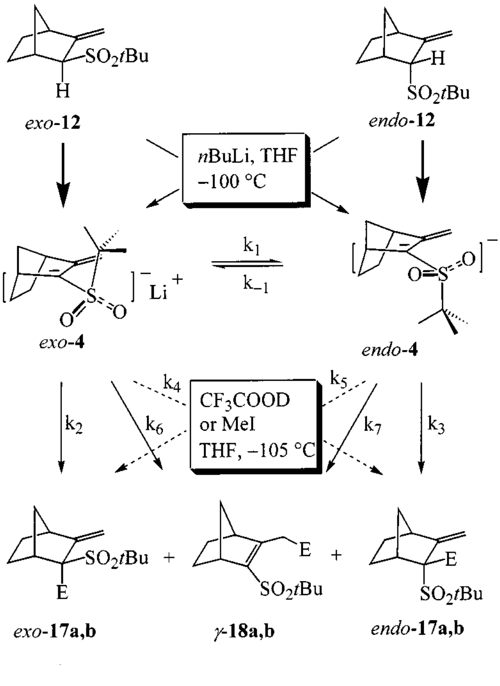


Figure 16. Structure of *exo*-**13c** in the crystal.

The generation and reactions of *exo*-**4** and *endo*-**4** with electrophiles were not as extensively studied as in the case of **3** because of the low α,γ-selectivity (Scheme 8, Table 15). Here, too, deuteration experiments were carried out, and showed that deprotonation of *endo*-**11** and *exo*-**11** at −78 °C with *n*BuLi was fast. Treatment of *exo*-**11** and *endo*-**11** at −78 °C with *n*BuLi in THF, followed by addition of ten equivalents of CF_3COOD after t_{isn} = 30 min, in both cases delivered mixtures of *endo*-**17a**, *exo*-**17a**, and γ-**18a**, in ratios of 5:54:51 and 6:49:45, respectively (Table 15, entries 1 and 2). Analogous treatment of the sulfones *exo*-**11** and *endo*-**11** with *n*BuLi at −78 °C, followed by addition of ten equivalents of MeI after t_{isn} = 30 min, in both cases gave mixtures of *endo*-**17b**, *exo*-**17b**, and γ-**18b**, both in ratios of approximately 0:14:86. Thus, methylation of *endo*-**4** and



Scheme 8. Synthesis and reactivity of *endo*-**4** and *exo*-**4**.

Table 15. Treatment of carbanion salt **4** with CF_3COOD and MeI at −78 °C in THF with formation of sulfones *endo*-**17a**,**b**, *exo*-**17a,b**, and γ-**18a**,**b**.

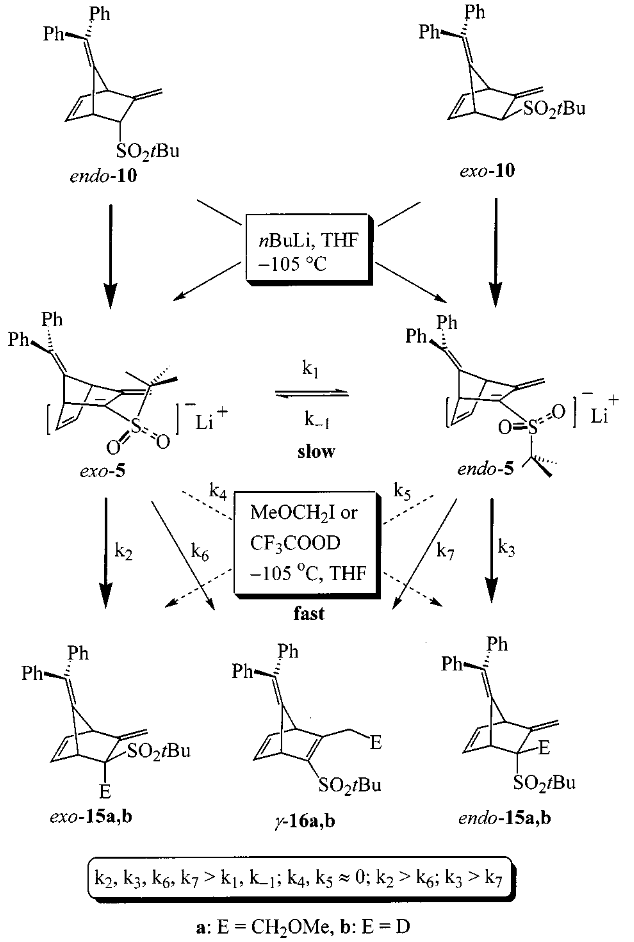
Entry	Startingmaterial **12**	Electrophile	t_{isn} (min)	Products *endo*:*exo*:γ [a]	Yield (%)
1	*endo*	CF_3COOD	30	5:54:41	89
2	*exo*	CF_3COOD	30	6:49:45	95
3	*endo*	MeI	30	0:15:85	90
4	*exo*	MeI	30	0:14:86	90

[a] According to GC.

exo-**4** proceeds with an α,γ-selectivity even lower than that of deuteration. The rate of methylation of **4** at this temperature is lower than that of *endo*-*exo* isomerization and the kinetics should thus approach the C−H limit. However, deuteration at this temperature most probably competes in rate with *endo*-*exo* isomerization: i.e., k_2, $k_3 \approx k_1$, k_{-1}. In both cases, interpretation of the stereoselectivities is hampered because of the low α,γ-selectivities: the large amounts of the alkenes γ-**18a** and γ-**18b** that are formed. At the C−H limit, the methylation of the unsaturated *S*-*tert*-butyl-substituted carbanion salt **3** with MeI occurred with a α,γ-selectivity of 93:7, while that of the saturated *S*-*tert*-butyl-substituted carbanion salt **4** proceeded with an opposite α,γ-selectivity of 15:85. What is the reason for this opposite behavior? The major structural difference between **3** and **4** is the saturation of C(5) and C(6) in the latter and, as a consequence, the additional H atoms in the *endo* positions. In comparison with that of methylation of *endo*-**3**, the TS of *exo* attack at the C(2) atom in *endo*-**4** should be disfavored because of an additional destabilizing interaction between the sulfonyl group and 6-H_{endo}. However, the TS of *endo* attack at the C(2) atom in *exo*-**4** should also be disfavored compared to that in *exo*-**3**, because of the interference of the trajectory of the electrophile with 6-H_{endo}. As a consequence of both effects, γ-attack dominates in the case of **4**.

The investigation of the reactivities of *endo*-**5** and *exo*-**5** was hampered by the limited accessibility of *endo*-**10** and *exo*-**10** in diastereomerically pure form. Thus, the deprotonation, methoxymethylation, and deuteration experiments were carried out by using 2.6:1 and 3:1 mixtures of the *endo* and *exo* sulfones (Scheme 9).

Deuteration experiments revealed that deprotonation of *endo*-**10** and *exo*-**10** with *n*BuLi at −100 °C was fast and complete within short time. Treatment of a 2.6:1 mixture of *endo*-**10** and *exo*-**10** with *n*BuLi at −105 °C in THF, followed by addition of ten equivalents of $MeOCH_2I$, gave after a short t_{isn} a mixture of the sulfones *endo*-**15a**, *exo*-**15a**, and γ-**16a** in a ratio of 21:70:9, in quantitative yield (Table 16, entry 1). The reactivity of $MeOCH_2I$ towards *endo*-**5** and *exo*-**5** at −105 °C was such that alkylation was complete within five minutes. Here, too, an increase in t_{isn} saw a change in the ratio of the sulfones, from mainly *exo* sulfone to mainly *endo* sulfone. In a final experiment, a solution of a mixture of *endo*-**5** and *exo*-**5** was allowed to warm to room temperature in order to ensure complete equilibration and subsequently quenched with the iodide at



Scheme 9. Synthesis and reactivity of *endo*-**5** and *exo*-**5**.

Table 16. Treatment of carbanion salt **5** with $MeOCH_2I$ at −105 °C in THF with formation of sulfones *endo*-**15a**, *exo*-**15a**, and γ-**16a**.

Entry	Starting material **10**	t_{isn} (min)	Products *endo*:*exo*:γ[a]	Yield (%)
1	*endo*:*exo* = 2.6:1	1.5	21:70:9	98
2	*endo*:*exo* = 2.6:1	15	29:62:9	98
3	*endo*:*exo* = 2.6:1	45	35:56:9	98
4	*endo*:*exo* = 2.6:1	120[b]	68:27:5	98

[a] According to GC. − [b] The solution was allowed to warm to room temperature and quenched at −105 °C.

−105 °C. In this case, a mixture of the sulfones *endo*-**15a**, *exo*-**15a**, and γ-**16a** in an opposite ratio of 68:27:5 was isolated (Table 16, entry 4). The configurations of *endo*-**15a** and *exo*-**15a** were assigned on the basis of NOE experiments and by comparison of their NMR spectroscopic data with those of *endo*-**10** and *exo*-**10**.

The obtained stereoselectivities of the deprotonation of the sulfones and of the methoxymethylation of *endo*-**5** and *exo*-**5** at −105 °C, and their dependence on t_{isn}, show that reaction with the electrophile and *endo*-*exo* isomerization approach kinetic quenching and thus parallel those of **3**. Especially revealing is the ratio of the *endo* and *exo* sulfones recorded in the case in which the approximately 2:1 equilibrium ratio of *endo*-**5** and *exo*-**5** at −105 ° C was established before quenching (*cf.* Table 16, entry 4). This ratio corresponds approximately to the 2:1 ratio of the diastereomers. These results can tentatively be explained in a similar manner as the case of **3**: the *endo* sulfone *endo*-**10** is selectively converted by the deprotonation-quenching sequence to the *exo* sulfone *exo*-**15a**, while the *exo* sulfone *exo*-**10** is selectively converted into the *endo* sulfone *endo*-**15a**. From these results, the following explanation of the selectivities is offered on the basis of the selectivity model put forward for *endo*-**3** and *exo*-**3** (*cf.* Scheme 6). Sulfone *endo*-**10** is highly selectively deprotonated with *n*BuLi, with formation of *exo*-**5**, which in turn reacts highly selectively, from the *endo* side, with $\mathrm{MeOCH_2I}$ to give sulfone *exo*-**15a** ($k_2 > k_4$). In a similar manner, the sulfone *exo*-**10** reacts highly selectively with *n*BuLi with formation of *endo*-**5**, which is attacked highly selectively from the *exo* side by $\mathrm{MeOCH_2I}$ to give sulfone *endo*-**15a** ($k_3 > k_5$).

Next, deuteration of *endo*-**5** and *exo*-**5** was investigated. Treatment of the 3:1 mixture of *endo*-**10** and *exo*-**10** with *n*BuLi at −105 °C in THF, followed by addition of ten equivalents of $\mathrm{CF_3COOD}$, furnished a mixture of *endo*-**15b**, *exo*-**15b**, and γ-**16b** in a ratio of 20:67:13 and in 93% yield (Table 17, entry 1). An increase in t_{isn} saw a slow increase in the *endo* sulfone and a decrease in the *exo* sulfone. In a final experiment, the solution of the mixture of *endo*-**5** and *exo*-**5** was allowed to warm to room temperature in order to ensure complete *endo*-*exo* equilibration and subsequently quenched with $\mathrm{CF_3COOD}$ at −105 °C. In this case a mixture of the sulfones *endo*-**15b**, *exo*-**15b**, and γ-**16b** in an opposite ratio of 51:36:13 was isolated (Table 17, entry 5). The results obtained in the deuteration of *endo*-**5** and *exo*-**5** parallel those of the methoxymethylation and also indicate kinetic quenching.

Table 17. Treatment of carbanion salt **5** with $\mathrm{CF_3COOD}$ at −105 °C in THF with formation of sulfones *endo*-**15b**, *exo*-**15b**, and γ-**16b**.

Entry	Starting material **10**	t_{isn} (min)	Products *endo*:*exo*:γ[a]	Yield (%)
1	*endo*:*exo* = 3:1	1	20:67:13	93
2	*endo*:*exo* = 3:1	10	21:67:12	93
3	*endo*:*exo* = 3:1	30	28:57:15	99
4	*endo*:*exo* = 3:1	60	33:50:17	99
5	*endo*:*exo* = 3:1	120[b]	51:36:13	99

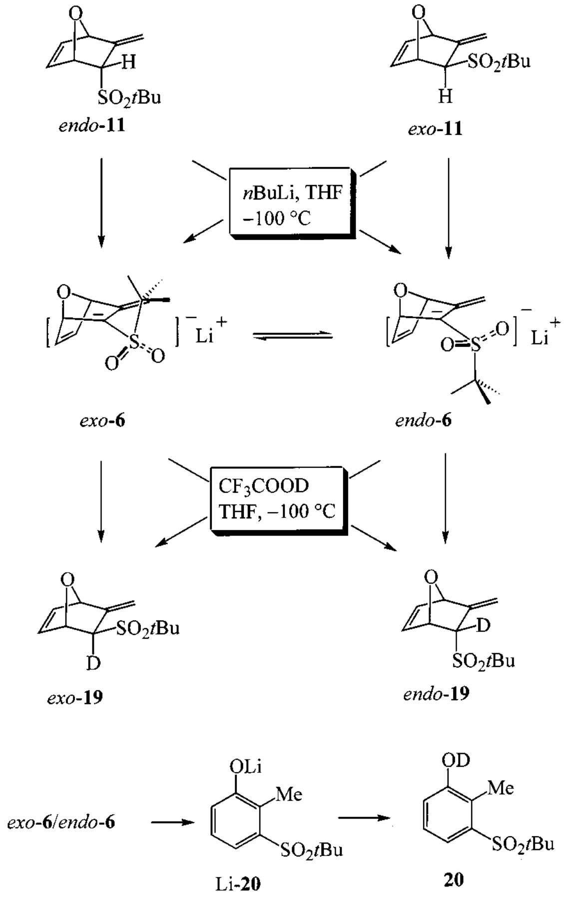
[a] According to GC and ^{1}H NMR spectroscopy. – [b] The solution was allowed to warm to room temperature and quenched at −105 °C.

Investigation of the regio- and stereoselectivity of **6** was obscured by its fast ring-opening reaction. Treatment of *endo*-**11** with *n*BuLi at −100 °C in THF, followed by addition of ten equivalents of $\mathrm{CF_3COOD}$, afforded a mixture of *endo*-**19** and *exo*-**19** in a ratio of 35:63, in admixture with

Table 18. Treatment of carbanion salt **6** with $\mathrm{CF_3COOD}$ at −105 °C in tetrahydrofuran with formation of sulfones *endo*-**19** and *exo*-**19**.

Entry	Starting material **11**	t_{isn} (min)	Products *endo*:*exo*:*rearr.*[a]	Yield (%)
1	*endo*	0.25	35:63:2	85
2	*endo*	0.5	33:64:3	65
3	*endo*	5	30:48:22	70
4	*endo*	10	28:33:39	76
5	*endo*	120[b]	0:0:100	68
6	*endo*[c]	5	37:44:19	87

[a] According to GC. – [b] The solution was allowed to warm to room temperature and quenched at −105 °C. – [c] A 2:1 mixture of *endo*-**11** and *exo*-**11** was used.



Scheme 10. Synthesis and reactivity of *endo*-**6** and *exo*-**6**.

2% of sulfone **20** (Table 18, Scheme 10). An increase in t_{isn} saw not only a change in the isomer ratio, but at the same time a significant increase in **20**. Interpretation of these results is hampered because of the lack of information concerning the structure and dynamic behavior of **6** and because of its competing rearrangement. It seems, however, that, in accordance with the behavior of the other *endo* sulfones and the corresponding *exo* carbanion salts, deprotonation of *endo*-**11** preferentially gives *exo*-**6**, which reacts with the electrophile selectively from the *endo* side to yield *exo*-**19** preferentially. Aside from the question of stereoselectivity, these results unequivocally show that carbanion salt **6** cannot only be generated at low temperatures but also has a half-life sufficient to allow reaction with reactive electrophiles.[36,37]

Conclusion

NMR spectroscopy of the allylic α-*tert*-butylsulfonyl carbanion salts **3**−**5**, possessing conformationally constrained C(2)−C(3) bonds and conformationally restricted C(2)−S bonds, at very low temperatures in THF solution has for the first time allowed the study not only of their *endo* and *exo* C(2)−S diastereomers, but also of their monomers and dimers. The *endo*-*exo* diastereomerization barriers in **3** and **5** are comparable in magnitude to those found for the enantiomerization of the lithium salts of benzylic *tert*-butylsulfonyl carbanions. The crystal structures of *exo*-**3**·PMDETA and *endo*-**1**/*ent*-*endo*-**1** can serve as reasonable models for the structures of monomeric and dimeric O−Li CIPs of **3**−**5** in solution. However, because of the possibility of fast equilibria between the various monomeric CIPs in solution, nothing can be said, on the basis of the results obtained, about the existence and structure of a CIP also featuring C−Li bonds as well as O−Li bonds. The NMR spectroscopic and crystallographic data point to additional stabilization of **3**−**5** by allylic delocalization of the negative charge. This is in accordance with results previously found for *S*-phenyl-substituted carbanion salts **1** and **2**, as well as for other lithium salts of acyclic allylic α-sulfonyl carbanions. The most significant structural difference between the *S*-phenyl- and the *S*-*tert*-butyl-substituted bicyclic allylic α-sulfonyl carbanions is the planarity of the anionic C(2) atoms in the latter, which is probably a result of the steric bulkiness of the *tert*-butyl group.

Kinetic quenching revealed not only stereoselective deprotonation of the sulfones, but also considerable asymmetric induction by the *tert*-butylsulfonyl group in reactions between the diastereomeric *endo* and *exo* carbanion salts **3**−**5** and electrophiles. Interpretation of their observed selectivities is hampered, however, since they are averages of the individual selectivities of the diastereomers, monomers, dimers, and CIPs, which may be different, and their discussion on the basis of kinetic quenching or the C−H limit is certainly an oversimplification.

The results obtained with *endo*-**3**−**5** and *exo*-**3**−**5** suggest that the enantiomerization barriers and stereoselectivities of the lithium salts of the acyclic allylic α-sulfonyl carbanions **II**/*ent*-**II** might be sufficient to justify further studies aimed at their enantioselective synthesis.[8]

Experimental Section

General: All reactions were carried out in absolute solvents under argon atmosphere with syringe and Schlenk techniques in oven-dried glassware. Solutions of the carbanion salts for NMR spectroscopy were sealed in oven-dried NMR tubes under argon. THF and ether were distilled under argon from potassium/benzophenone and sodium/benzophenone, respectively. Toluene was distilled from sodium, and MeOH was dried with magnesium and distilled. NEt_3, PMDETA, and CH_2Cl_2 were distilled from calcium hydride. ^{6}Li-*n*Pr was prepared as described in the literature.[38] − ^{1}H, ^{13}C NMR, and ^{6}Li spectra were recorded on Varian VXR 300, Varian Gemini 300, Varian Inova 400, and Varian Unity 500 spectrometers. The following parameters were used for the HOESY experiments: mixing time 1 s, relaxation delay 4.2 s, repetitions 320, increments 2×64. The ROESY experiments were carried out by using the following parameters: mixing time 0.20 s, repetitions 8, increments 128×2. ^{1}H and ^{13}C chemical shifts are reported relative to TMS. Splitting patterns in the ^{1}H NMR spectra are designated as: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quadruplet; quin, quintet; m, multiplet. NMR chemical shifts of minor isomers obtained only as a mixture with the major isomers are given only when an unequivocal assignment was possible. − GC analyses were performed by using Chrompack CP-9000 instruments (CP-Sil-8: 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). − GC MS analyses were run on a Magnum Finnigan (HT-5: 25 m, 0.25 mm; 50 kPa He, CI, 40 eV, MeOH). − MS spectra were recorded on a Varian MAT 212S (EI, 70 eV). Only decisive MS signals and those with an intensity higher than 10% are listed. − IR spectra were recorded on a Perkin−Elmer FT 1760 instrument. Only peaks of $\tilde{\nu} > 700$ cm^{-1} are listed. − Column chromatography was carried out on Merck silica gel 60, 0.063−0.200 mm. − TLC was performed with Merck silica gel 60 F_{254} plates. − Preparative HPLC was run with a Merck Nova Prep 200 instrument, using a Hibar pre-packed 250/25 column filled with LiChrospher Si 60 (7 μ), cyclohexane/ethyl acetate, 8:1, flow 15 mL/min, UV 254 nm. − Elemental analyses were carried out by the microanalytical laboratory of the Institut für Organische Chemie.

X-ray Analysis: The crystal structures of *exo*-**3**·PMDETA, *exo*-**9**, and *exo*-**13c** were solved using direct methods as implemented in the XTAL3.2 package of crystallographic routines,[39] employing GENSIN to generate structure-invariant relationships and GENTAN for the general tangent phasing procedure. The crystal data and the most salient experimental parameters used in the X-ray measurements and in the crystal structure analyses are reported in Table 19. The structures were viewed with the program SCHAKAL92.[40]

Cryoscopy: The cryoscopic experiments were carried out by the method of Bauer and Seebach[27] as described for **1** and **2** in ref.[7] THF: m.p. 164.566 ± 0.0016 K, $E_K = 1.856 \pm 0.016$ K·kg/mol.

Prop-2-ynyl 2-Methylpropane-2-sulfinate (7): A solution of 2-methylpropane-2-sulfinyl chloride (57.6 g, 0.42 mol) in CH_2Cl_2

Table 19. Crystal data and parameters of data collection for carbanion salts *exo*-**3**·PMDETA, sulfone *exo*-**9**, and sulfone *exo*-**13c**

Compound	*exo*-**9**	*exo*-**3**·PMDETA	*exo*-**13c**
(a) Crystal data			
formula	$C_{12}H_{18}O_2S$	$C_{21}H_{40}LiN_3O_2S$	$C_{13}H_{20}O_2S$
M_r	226.34	405.57	240.37
crystal size, ca. mm	0.3 × 0.3 × 0.3	0.5 × 0.5 × 0.5	0.3 × 0.3 × 0.3
crystal system	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	$P2_12_12_1$ (No. 19)
a, Å	9.516(3)	14.732(1)	6.116(2)
b, Å	11.196(2)	16.616(1)	12.660(2)
c, Å	12.194(1)	19.835(3)	16.380(2)
α, deg	92.64(1)	90.0	90.0
β, deg	101.42(1)	90.0	90.0
γ, deg	106.28(1)	90.0	90.0
V, $Å^3$	1215.24	4855.5	1268.3
Z	4	8	4
$D_{calcd.}$, g cm^{-3}	1.237	1.110	1.259
μ, cm^{-1}	21.57	12.87	20.88
(b) data collection			
diffractometer	CAD4	CAD4	CAD4
T, °C	25	−93	−123
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}, deg	75.2	75.2	75.2
no. of data colld	10149	5690	3184
no. of unique data	4960	5531	2378
obsn criterion	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$	$I > 2\ \sigma(I)$
no. of data obsd	3586	3802	2007
(c) refinement			
no. of params refd	271	253	172
R, R_w [a]	0.068, 0.080	0.087, 0.079	0.069, 0.079
extinction, *r**	not refined	not refined	not refined
Δ(ρ), e $Å^{-3}$	−0.6/+0.5	−1.6/+1.3	−0.45/+1.05
GOF	3.348	1.920	

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

(400 mL) was added dropwise at 0 °C to a solution of propargyl alcohol (24.7 mL, 0.42 mol) and NEt_3 (68 mL, 0.49 mol) in CH_2Cl_2 (1100 mL). The mixture was stirred at 0 °C for 30 min, allowed to warm to room temperature, and diluted with CH_2Cl_2 (1000 mL). The organic phase was washed successively with 10% H_2SO_4 (2000 mL), saturated aqueous $NaHCO_3$ (2000 mL), and H_2O (2000 mL), dried ($MgSO_4$), and concentrated in vacuo to give **7** (61.9 g, 92%) as a yellow-orange oil. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9 H, CMe_3), 2.57 (t, $J_{3,1}$ = 2.3 Hz, 1 H, 3-H), 4.66 (d, $J_{1,3}$ = 2.3 Hz, 2 H, 1-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.54 (C*Me*$_3$), 56.21 (C-1), 57.76 (*C*Me$_3$), 76.28 (C-3), 77.89 (C-2). − GC MS: *m*/*z* (%) = 160 [M^+] (16), 104 (3), 90 (4), 89 (100), 70 (8), 61 (34), 57 (26), 55 (6). − $C_7H_{12}O_2S$ (160.2): calcd. C 52.47, H 7.55; found C 52.32, H 7.61.

1-(2-Methylpropyl-2-sulfonyl)propa-1,2-diene (8): A solution of **7** (61.9 g, 0.39 mol) in chlorobenzene (2500 mL) was heated to reflux for 16 h. Evaporation of the solvent left a dark brown solid, which was dissolved in ether (400 mL). The solution was filtered and kept at 2 °C for 24 h until complete crystallization. Filtration and drying in vacuo furnished **8** (41.1 g, 67%) as a light yellow solid. − M.p. 79 °C. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, CMe_3), 5.47 (d, $J_{3,1}$ = 6.4 Hz, 2 H, 3-H), 6.08 (t, $J_{1,3}$ = 6.4 Hz, 1 H, 1-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.35 (C*Me*$_3$), 60.80 (*C*Me$_3$), 82.68 (C-3), 93.16 (C-1), 211.98 (C-2). − GC MS: *m*/*z* (%) = 160 [M^+] (25), 105 (88), 97 (14), 89 (43), 81 (5), 69 (4), 61 (9), 57 (100). − $C_7H_{12}O_2S$ (160.2): calcd. C 52.47, H 7.55; found C 52.26, H 7.59.

***endo*- and *exo*-3-Methylene-2-(2-methylpropyl-2-sulfonyl)-bicyclo[2.2.1]hept-5-ene (*endo*-9 and *exo*-9):** A solution of **8** (12.8 g, 0.08 mol) and cyclopentadiene (34.7 mL, 0.42 mol) in toluene (400 mL) was heated to reflux for 17 h. Evaporation of the solvent gave a mixture of *endo*-**9** and *exo*-**9** in a ratio of 1.4:1, as a yellow-brown oil. Chromatography (EtOAc/*n*-hexane, 1:2) and crystallization from EtOAc/*n*-hexane, 1:1, afforded *endo*-**9** (7.8 g, 43%) and *exo*-**9** (7.4 g, 41%) as colorless crystals. ***endo*-9**: M.p. 91−92 °C. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 9 H, CMe_3), 1.55 (dm, $J_{7s,7a}$ = 8.7 Hz, 1 H, 7-H_s), 1.69 (dm, $J_{7a,7s}$ = 8.7 Hz, 1 H, 7-H_a), 3.33 (sm, 2 H, 1-H, 4-H), 4.25 (dd, $J_{2,8a/s}$ = 2.4, $J_{2,8a/s}$ = 2.0 Hz, 1 H, 2-H), 5.28 (d, $J_{8a/s,2}$ = 2.0 Hz, 1 H, 8-$H_{a/s}$), 5.29 (d, $J_{8a/s,2}$ = 2.4 Hz, 1 H, 8-$H_{a/s}$), 6.29 (st, 2 H, 5-H, 6-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.82 (C*Me*$_3$), 46.90 (C-1), 49.80 (C-7), 51.95 (C-4), 60.34 (*C*Me$_3$), 61.80 (C-2), 110.40 (C-8), 134.01 (C-6), 135.30 (C-5), 144.18 (C-3). − MS: *m*/*z* (%) = 226 [M^+] (5), 170 (17), 161 (4), 122 (3), 106 (18), 105 (66), 103 (12), 91 (19), 79 (23), 78 (9), 77 (15), 66 (10), 57 (100), 41 (29), 39 (12). − $C_{12}H_{18}O_2S$ (226.3): calcd. C 63.68, H 8.02, found C 63.46, H 8.02. ***exo*-9**: M.p. 77−78 °C. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 9 H, CMe_3), 1.70 (dm, $J_{7a,7s}$ = 9.1 Hz, 1 H, 7-H_a), 2.08 (dm, $J_{7s,7a}$ = 9.1 Hz, 1 H, 7-H_s), 3.30 (s, 1 H, 1-H), 3.39 (s, 1 H, 4-H), 3.57 (dd,

$J_{2,8a}$ = 2.4, $J_{2,8s}$ = 1.7 Hz, 1 H, 2-H), 5.29 (d, $J_{8s,2}$ = 1.7 Hz, 1 H, 8-H$_s$), 5.39 (d, $J_{8a,2}$ = 2.4 Hz, 1 H, 8-H$_a$), 6.18 (dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 6.35 (dd, $J_{6,5}$ = 5.7, $J_{6,1}$ = 3.0 Hz, 1 H, 6-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.06 (C*Me*$_3$), 47.59 (C-1), 48.19 (C-7), 49.62 (C-4), 59.97 (C-2), 61.07 (*C*Me$_3$), 112.42 (C-8), 134.73 (C-6), 140.56 (C-5), 143.05 (C-3). − MS: *m*/*z* (%) = 226 [M$^+$] (2), 170 (11), 161 (16), 106 (28), 105 (100), 103 (17), 91 (32), 79 (31), 78 (12), 77 (17), 66 (14), 57 (75), 41 (12). − $C_{12}H_{18}O_2S$ (226.3): calcd. C 63.68, H 8.02, found C 63.59, H 7.92.

***endo*- and *exo*-Benzhydrylidene-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-10 and *exo*-10):** A solution of **8** (5.6 g, 35 mmol) and diphenylfulvene (9.67 g, 42 mmol) in toluene (200 mL) was heated to reflux. After 24 h the mixture was concentrated in vacuo and the residual red-orange oil was purified by chromatography (*n*-hexane/EtOAc, 2:1). Crystallization of the residue from *n*-hexane/EtOAc, 8:1, furnished a 2.6:1 mixture of *endo*-**10** and *exo*-**10** (9.9 g, 72%) as colorless crystals. Preparative HPLC of the 2.6:1 mixture of *endo*-**10** and *exo*-**10** (225 mg) gave oily *exo*-**10** (15 mg), which crystallized upon standing at room temperature, crystalline *endo*-**10** (107 mg) and a mixture of *endo*-**10** and *exo*-**10** (90 mg) containing an impurity. − R_f (*endo*-**10**/*exo*-**10**) = 0.40 (*n*-hexane/EtOAc, 2:1). ***endo*-10**: M.p. 154 °C. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.43 (s, 9 H, CMe$_3$), 3.82 (br. s, 1 H, 1-H), 3.89 (q, *J* = 1.8 Hz,1 H, 4-H), 4.43 (dt, *J* = 3.3, *J* = 2.2 Hz, 1 H, 2-H), 5.34 (m, 2 H, 8-H$_{a/s}$), 6.52 (m, 2 H, 5-H, 6-H), 7.05−7.35 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 24.14 (C*Me*$_3$), 49.46 (C-1/4), 54.29 (C-1/4), 60.79 (*C*Me$_3$), 61.66 (C-2), 111.10 (C-8), 123.92 (C-7), 127.36 and 127.45 (*p*-C), 128.31, 128.40, 129.68 and 129.83 (*o*-, *m*-C) 134.58 (C-5/6), 135.99 (C-5/6), 140.40 and 140.45 (*i*-C), 142.43 (C-9), 148.94 (C-3). − IR (KBr): $\tilde{\nu}$ = 3050 (w), 3020 (w), 2984 (w), 2970 (w), 2930 (e), 1735 (w), 1685 (w), 1650 (w), 1600 (w), 1490 (m), 1475 (w), 1441 (m), 1305 (s), 1115 (s), 930 (m), 746 (s), 710 (s) cm^{-1}. − MS; *m*/*z* = 390 [M$^+$] (10), 334 (64), 316 (20), 299 (18), 269 (100), 268 (44), 254 (50), 253 (36), 241 (20), 239 (20), 228 (20), 215 (10), 202 (8), 191 (75), 189 (20), 178 (7), 165 (34), 152 (9), 141 (5), 115 (8), 91 (50). − $C_{25}H_{26}O_2S$ (390.5): calcd. C 76.89, H 6.71; found C 76.84, H 6.63. − ***exo*-10:** M.p. 196−197 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.18 (s, 9 H, CMe$_3$), 3.73 (br. s, 1 H, 2-H), 3.79 (br. s, 1 H, 1-H), 3.96 (br. s, 1 H, 4-H), 5.47 (br. s, 1 H, 8-H$_a$), 5.55 (ds, 1 H, 8-H$_s$), 6.44 (dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 6.54 (dd, $J_{6,5}$ = 5.7, $J_{6,1}$ = 3.0 Hz, 1 H, 6-H), 7.11−7.32 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.24 (C*Me*$_3$), 47.67 (C-1/4), 52.92 (C-1/4), 61.42 (*C*Me$_3$), 62.96 (C-2), 112.23 (C-8), 126.47 (C-7), 126.78 and 126.88 (*p*-C), 127.76, 127.99, 129.86 and 129.97 (*o*-, *m*-C), 133.72 (C-5/6), 139.85 (C-9), 140.78 and 141.15 (*i*-C), 142.13 (C-5/6), 147.65 (C-3). − IR (KBr): $\tilde{\nu}$ = 3050 (w), 3027 (w), 2985 (m), 2970 (m), 2933 (w), 2872 (w), 1685 (w), 1649 (w), 1597 (w), 1477 (m), 1461 (m), 1442 (m), 1396 (w), 1367 (w), 1296 (s), 1244 (w), 1215 (m), 1192 (w), 1173 (m), 1142 (w), 1114 (s), 1075 (m), 1027 (m), 929 (w), 903 (m), 877 (m), 771 (m), 759 (m), 743 (s), 720 (w), 705 (s) cm^{-1}. − MS: *m*/*z* (%) = 390 [M$^+$] (23), 334 (42), 316 (44), 299 (47), 269 (97), 268 (100), 254 (64), 253 (64), 241 (26), 239 (33), 228 (33), 215 (23), 202 (17), 191 (94), 189 (54), 178 (13), 165 (55), 152 (15), 141 (7), 115 (11), 91 (35), 78 (4), 57 (51). − $C_{25}H_{26}O_2S$ (390.5): calcd. C 76.89, H 6.71; found C 76.55, H 6.81.

***endo*- and *exo*-3-Methylene-2-(2-methylpropyl-2-sulfonyl)-7-oxabicyclo[2.2.1]hept-5-ene (*endo*-11 and *exo*-11):** A solution of **8** (2.4 g, 15 mmol) and furan (5.4 mL, 75 mmol) in toluene (75 mL) was heated to reflux for 30 h. A second portion of furan (5 mL) was added and heating to reflux was continued for 55 h. The volatiles were subsequently removed in vacuo and the residual orange oil was purified by chromatography (*n*-hexane/EtOAc, 1:1). The colorless solid thus obtained was crystallized from *n*-hexane/EtOAc, 3:1, to yield *endo*-**11** (2.08 g, 61%) as colorless crystals. Workup of the mother liquor furnished a 2:1 mixture of *endo*-**11** and *exo*-**11** (400 mg, 12%) as colorless crystals, m.p. 85−87 °C. − ***endo*-11:** M.p. 102−103 °C. − R_f = 0.38 (*n*-hexane/EtOAc, 1:1). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.47 (s, 9 H, CMe$_3$), 4.37 (pm, $J_{2,8a/s}$ = 2.4, $J_{2,8a/s}$ = 1.8 Hz, 1 H, 2-H), 5.14 (br. s, 1 H, 4-H), 5.24 (sd, 1 H, 1-H), 5.36 (d, $J_{8a/s,2}$ = 1.8 Hz, 1 H, 8-H$_{a/s}$), 5.37 (d $J_{8a/s,2}$ = 2.4 Hz, 1 H, 8-H$_{a/s}$), 6.57 (dd, $J_{6,5}$ = 5.8, $J_{6,1}$ = 1.5 Hz, 1 H, 6-H), 6.62 (dd, $J_{5,6}$ = 5.8, $J_{5,4}$ = 1.8 Hz, 1 H, 5-H). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 23.62 (C*Me*$_3$), 59.32 (C-2), 60.34 (*C*Me$_3$), 80.36 (C-1/4), 83.94 (C-1/4), 110.88 (C-8), 134.08 (C-5/6), 135.40 (C-5/6), 139.70 (C-3). − IR (KBr): $\tilde{\nu}$ = 3090 (w), 3025 (m), 2996 (w), 2968 (m), 2956 (m), 2937 (m), 2910 (m), 2874 (m), 1662 (m), 1571 (w), 1438 (m), 1465 (m), 1427 (w), 1399 (m), 1372 (s), 1314 (s), 1293 (s), 1271 (s), 1245 (m), 1217 (m), 1198 (m), 1143 (m), 1113 (s), 1081 (m), 1022 (s), 978 (m), 963 (s), 914 (s), 890 (s), 867 (s), 821 (s), 803 (s), 779 (m), 730 (s) cm^{-1}. − MS (70 eV): *m*/*z* (%) = 228 [M$^+$] (1), 172 (2), 155 (1), 127 (1), 123 (11), 108 (9), 107 (13), 95 (6), 80 (11), 79 (45), 78 (11), 77 (32), 68 (13), 57 (100), 51 (9). − $C_{11}H_{16}O_3S$ (228.3): calcd. C 57.87, H 7.06; found C 57.87, H 7.13. − ***exo*-11:** R_f = 0.32 (*n*-hexane/EtOAc, 1:1). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.48 (s, 9 H, CMe$_3$), 3.60 (tm, 1 H, 2-H), 5.20 (br. s, 1 H, 4-H), 5.43 (sm, 1 H, 1-H), 5.47 (br. s, 1 H, 8-H$_a$), 5.55 (br. s, 1 H, 8-H$_s$), 6.43 (dd, $J_{6,5}$ = 5.5, $J_{6,1}$ = 1.8 Hz, 1 H, 6-H), 6.58 (dd, $J_{5,6}$ = 5.5, $J_{5,4}$ = 1.5 Hz, 1 H, 5-H). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 24.36 (C*Me*$_3$), 63.49 (*C*Me$_3$), 64.34 (C-2), 81.27 (C-1/4), 81.92 (C-1/4), 112.41 (C-8), 134.33 (C-5/6), 137.92 (C-3), 138.23 (C-5/6). − ***endo*-11/*exo*-11 (2:1):** $C_{11}H_{16}O_3S$ (228.3): calcd. C 57.87, H 7.06; found C 57.75, H 7.15.

***endo*-3-Methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]heptane (*endo*-12):** A mixture of *endo*-**9** (1.0 g, 4.4 mmol) and Pd/C (10%) (1.0 g) in MeOH (60 mL) was vigorously stirred under an atmosphere of hydrogen at room temperature at slightly elevated pressure in a hydrogenation apparatus. After a reaction time of 29 min, 115 mL of hydrogen had been taken up and hydrogenation was terminated by removal of the catalyst by filtration through Celite. Concentration of the solution in vacuo and chromatography (*n*-hexane/EtOAc, 2:1) of the residue gave *endo*-**12** (756 mg, 75%) as a colorless solid. − M.p. 84 °C. − R_f = 0.35 (*n*-hexane/EtOAc, 2:1). − ^{1}H NMR (500 MHz, CDCl$_3$): δ **=** 1.46 (s, 9 H, CMe$_3$), 1.48 (sm, 3 H, 6-H$_{exo}$/7-H$_a$/7-H$_s$), 1.57 (m, 1 H, 5-H), 1.72 (m, 1 H, 5-H), 2.35 (m, 1 H, 6-H$_{endo}$), 2.80 (br. s, 1 H, 4-H), 2.85 (sd, 1 H, 1-H), 4.00 (m, 1 H, 2-H), 5.19 (d, $J_{8a,2}$ = 2.72 Hz, 1 H, 8-H$_a$), 5.43 (d, $J_{8s,2}$ = 2.1 Hz, 1 H, 8-H$_s$). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 22.98 (C-6), 24.14 (C*Me*$_3$), 28.48 (C-5), 39.77 (C-7), 41.53 (C-1), 46.43 (C-4), 60.97 (*C*Me$_3$), 63.53 (C-2), 109.51 (C-8), 146.10 (C-3). − IR (KBr): $\tilde{\nu}$ = 2956 (s), 2875 (s), 1658 (m), 1477 (s), 1462 (s), 1396 (m), 1371 (m), 1359 (m), 1289 (s), 1275 (s), 1245 (s), 1218 (m), 1191 (s), 1109 (s), 1017 (m), 969 (w), 916 (s), 865 (s), 840 (m), 802 (m), 773 (w), 737 (m) cm^{-1}. − MS (70 eV): *m*/*z* (%) = 228 [M$^+$] (1), 164 (3), 149 (2), 136 (4), 114 (4), 109 (10), 108 (15), 107 (25), 91 (10), 80 (32), 79 (50), 77 (13), 67 (7), 57 (100). − $C_{12}H_{20}O_2S$ (228.3): calcd. C 63.12, H 8.83; found C 63.09, H 8.64.

***exo*-3-Methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]heptane (*exo*-12):** A mixture of *exo*-**9** (1.0 g, 4.4 mmol) and Pd/C (10%) (1.0 g) in MeOH (60 mL) was vigorously stirred under an atmosphere of hydrogen at room temperature at slightly elevated pressure in a hydrogenation apparatus. After a reaction time of 26 min, 115 mL of hydrogen had been taken up and hydrogenation was terminated by removal of the catalyst by filtration through Celite. Concentration of the solution in vacuo and chromatography (*n*-hexane/EtOAc, 2:1) of the residue gave *exo*-**12** (603 mg, 60%) as a colorless solid. − M. p. 70 °C. − R_f = 0.38 (*n*-hexane/EtOAc, 2:1). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.30 (m, 1 H, 6-H$_{endo}$), 1.34 (dm, $J_{7a,7s}$ = 10.07 Hz, 1 H, 7-H$_a$), 1.40 (m, 1 H, 5-H$_{endo}$), 1.46 (s, 9 H, CMe$_3$), 1.72 (m, 2 H, 5-H$_{exo}$/6-H$_{exo}$), 1.99 (dm, $J_{7s,7a}$ = 10.0 Hz, 1 H, 7-H$_s$), 2.82 (br. s, 1 H, 1-H), 2.87 (br. s, 1 H, 4-H), 3.57 (m, 1 H, 2-H), 5.22 (d, $J_{8a,2}$ = 1.7 Hz, 1 H, 8-H$_a$), 5.33 (d, $J_{8s,2}$ = 2.3 Hz, 1 H, 8-H$_s$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.13 (C*Me*$_3$), 27.41 (C-6), 30.21 (C-5), 37.58 (C-7), 42.27 (C-1), 44.26 (C-4), 60.88 (CMe$_3$), 63.09 (C-2), 111.76 (C-8), 146.93 (C-3). − IR (KBr): ṽ = 3098 (w), 2978 (s), 2954 (s), 2926 (s), 2876 (s), 1654 (m), 1475 (s), 1452 (m), 1400 (m), 1369 (m), 1309 (s), 1286 (s), 1240 (m), 1196 (m), 1111 (s), 1038 (m), 929 (w), 905 (s), 895 (s), 868 (s), 845 (m), 801 (m), 765 (w), 738 (m) cm^{-1}. − MS (70 eV): *m*/*z* (%) = 228 [M$^+$] (1), 172 (2), 164 (5), 149 (3), 136 (6), 108 (23), 107 (38), 91 (11), 80 (54), 79 (75), 77 (19), 66 (8), 57 (100). − C$_{12}$H$_{20}$O$_2$S (228.3): calcd. C 63.12, H 8.83; found C 63.16, H 8.91.

Lithiumpentamethyldiethylenetriamine *exo*-3-Methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene-2-ide (*exo*-3·PMDETA): THF (0.8 mL) was added to a suspension of *endo*-**9** (208 mg, 0.92 mmol) in PMDETA (1.0 mL), whereupon the sulfone dissolved. The solution was treated with *n*BuLi (0.63 mL, 1.6 m in *n*-hexane, 1.01 mmol) at 0 °C, producing a colorless solid. Warming of the mixture to room temperature and addition of THF (3.1 mL) afforded a clear slightly yellow solution, which was kept at 2 °C for 8 days. Removal of the mother liquor and drying of the solid material in a stream of argon gave *exo*-**3**·PMDETA (316 mg, 85%) as colorless crystals. − ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 1.17 (s, 9 H, CMe$_3$), 1.40 (dm, $J_{7a,7s}$ = 5.8 Hz, 1 H, 7-H$_a$), 1.52 (s, 1 H, 7-H$_s$), 2.13 (s, 12 H, NMe$_2$), 2.18 (s, 3 H, NMe), 2.28 (m, 4 H, NCH$_2$), 2.39 (m, 4 H, NCH$_2$), 2.99 (s, 1 H, 4-H), 3.36 (s, 1 H, 1-H), 3.90 (d, *J* = 3.0 Hz, 1 H, 8-H$_a$), 3.93 (d, *J* = 2.8 Hz, 1 H, 8-H$_s$), 5.93 (sm, 1 H, 5-H), 6.23 (sm, 1 H, 6-H). − ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 25.56 (C*Me*$_3$), 43.24 (NMe), 46.08 (NMe), 49.78 (C-1), 57.23 (NCH$_2$), 57.82 (C-7), 58.65 (C-4), 58.73 (NCH$_2$), 60.71 (C-2), 63.61 (*C*Me$_3$), 80.24 (C-8), 131.88 (C-5), 139.34 (C-6), 155.80 (C-3).

Lithium *exo*-3-Methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo-[2.2.1]hept-5-ene-2-ide (3): *n*BuLi (0.63 mL, 1.6 m in *n*-hexane, 1.01 mmol) was added dropwise at −78 °C to a solution of *endo*-**9** (208 mg, 0.92 mmol) in THF (1.0 mL). After the colorless solution had been stirred for 10 min at this temperature, it was allowed to warm to room temperature and concentrated in vacuo to give **3**·(THF)$_n$ as a colorless solid. The material was dried under high vacuum and dissolved in [D$_8$]THF. − ^{1}H NMR (500 MHz, [D$_8$]THF): δ = 1.16 (br. s, 9 H, CMe$_3$), 1.40 (dm, $J_{7a,7s}$ = 5.80 Hz, 1 H), 1.52 (br. s, 1 H, 7-H$_s$), 2.99 (br. s, 1 H, 4-H), 3.35 (br. s, 1 H, 1-H), 3.93 (bd, *J* = 2.75 Hz, 1 H, 8-H$_a$), 3.95 (bd, *J* = 3.05 Hz, 1 H, 8-H$_s$), 5.93 (br. s, 1 H, 5-H), 6.22 (br. s, 1 H, 6-H). − ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 25.56 (C*Me*$_3$), 49.75 (C-1), 57.08 (C-7), 57.81 (C-4), 60.71 (C-2), 63.64 (*C*Me$_3$), 80.366 (C-8), 131.84 (C-5), 139.30 (C-6), 155.69 (C-3).

Lithium 3-Methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]-heptame-2-ide (4): *n*BuLi (0.16 mL of 1.60 m in *n*-hexane, 0.25 mmol) was added dropwise at −78 °C to a solution of *endo*-**12** (52.5 mg, 0.23 mmol) in THF (1.0 mL). After the colorless solution had been stirred for 10 min at this temperature, it was allowed to warm to room temperature and concentrated in vacuo to give **4**·(THF)$_n$ as a colorless solid. The material was dried under high vacuum and dissolved in [D$_8$]THF. − ^{1}H NMR (500 MHz, [D$_8$]THF): δ = 1.08 (dm, $J_{7a,7s}$ = 7.63 Hz, 1 H, 7-H$_a$), 1.24 (s, 9 H, CMe$_3$), 1.25 (m, 1 H, 5-H$_{endo}$), 1.46 (br. s, 1 H, 7-H$_s$), 1.55 (m, 2 H, 5-H$_{exo}$, 6-H$_{endo}$), 1.66 (m, 1 H, 6-H$_{exo}$), 2.51 (s, 1 H, 4-H), 2.81 (s, 1 H, 1-H), 3.44 (d, *J* = 3.1 Hz, 1 H, 8-H$_a$), 3.67 (d, *J* = 2.7 Hz, 1 H, 8-H$_s$). − ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 25.95 (C*Me*$_3$), 30.71 (C-5), 35.82 (C-6), 44.17 (C-7), 45.33 (C-1), 52.51 (C-4), 64.21 (C-2), 64.94 (CMe$_3$), 74.44 (C-8), 158.44 (C-3).

Lithium Benzhydrylidene-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-en-2-ide (5): *n*BuLi (0.14 mL of 1.60 m in *n*-hexane, 0.22 mmol) was added dropwise at −78 °C to a solution of *endo*-**10**/*exo*-**10** (3:1) (78 mg, 0.20 mmol) in THF (1.0 mL). After the deep yellow solution had been stirred for 10 min at this temperature, it was allowed to warm to room temperature and concentrated in vacuo to give **4**·(THF)$_n$ as an orange solid. The solid material was dried under high vacuum and dissolved in [D$_8$]THF. − ^{1}H NMR (500 MHz, [D$_8$]THF): δ = 1.11 (br. s, 9 H, CMe$_3$), 3.44 (tm, 1 H, 4-H), 3.90 (br. s, 1 H, 1-H), 3.99 (br. s, 1 H, 8-H$_a$), 4.03 (br. s, 1 H, 8-H$_s$), 6.21 (br. s, 1 H, 5-H), 6.57 (br. s, 1 H, 6-H), 7.05−7.20 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 25.47 (C*Me*$_3$), 51.80 (br, C-1), 60.23 (C-4), 63.32 (C-2), 63.73 (*C*Me$_3$), 78.95 (C-8), 112.10 (C-7), 125.90 and 125.96 (*p*-C), 127.96, 130.85 and 131.24 (*o*-, *m*-C), 135.03 (C-5), 138.45 (br, C-6), 142.88 and 143.28 (*i*-C), 153.04 (C-9), 159.20 (C-3).

General Procedure for the Synthesis of 3−6 and Their Treatment with Electrophiles: *n*BuLi (0.16 mL, 1.6 m in *n*-hexane, 0.25 mmol) was added dropwise at −78 °C or −105 °C to a solution of *endo*-**9**−**12** or *exo*-**9**−**12** (52 mg, 0.23 mmol) in THF (5 mL). After the colorless solution had been stirred for t_{isn}, the electrophile was added to the solution of **3**−**6** at the given temperature. After the solution had been stirred for t_{ren}, the mixture was quenched by addition of CF$_3$COOD, stirred for 10 min, and allowed to warm to room temperature over 1.5 h. Subsequently, saturated aqueous NaHCO$_3$ (20 mL) was added and the mixture was extracted with ether (20 mL). The combined organic phases were washed with saturated aqueous NaHCO$_3$ (40 mL), dried (MgSO$_4$), and concentrated in vacuo. Purification of the residue by chromatography (EtOAc/*n*-hexane) afforded a mixture of the corresponding sulfones as a colorless solid or as an oil.

***endo*- and *exo*-3-Methylene-2-methoxymethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-13a and *exo*-13a) and 3-(2-Methoxyethyl)-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]-hepta-2,5-diene (14a):** MeOCH$_2$I (0.20 mL, 2.3 mmol) was added to the solution of **3** at −105 °C after t_{isn}. Quenching with CF$_3$COOD after 5 min and workup gave a mixture of *endo*-**13a**, *exo*-**13a**, and **14a** as a colorless solid. ***endo*-13a:** t_R = 12.41 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.48 (s, 9 H, CMe$_3$), 1.61 (dm, $J_{7,7}$ = 9.1 Hz, 1 H, 7-H), 1.80 (dm, $J_{7,7}$ = 9.1 Hz, 1 H, 7-H), 3.31 (s, 1 H, 4-H), 3.32 (s, 3 H, CH$_3$), 3.60 (d, *J* = 11.8 Hz, 1 H, CH$_2$), 3.61 (s, 1 H, 1-H), 4.41 (d, *J* = 11.8 Hz, 1 H, CH$_2$), 5.19 (s, 1 H, 8-H$_{a/s}$), 5.43 (s, 1 H, 8-H$_{a/s}$), 6.16 (dd, $J_{6,5}$ = 5.4, $J_{6,1}$ = 3.0 Hz, 1 H, 6-H), 6.32 (dd, $J_{5,6}$ = 5.4, $J_{5,4}$ = 3.4 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.54 (C*Me*$_3$), 47.61 (C-1/4), 47.98 (C-7), 51.75 (C-1/4), 58.19 (CH$_3$), 66.12 (*C*Me$_3$), 75.33 (CH$_2$), 77.36 (C-2), 110.28 (C-8), 135.35 (C-5/6), 136.17 (C-5/6), 148.55 (C-3). − GC MS: *m*/*z* (%) = 270 [M$^+$] (1), 215 (3), 197 (4), 183 (5), 149 (100), 135 (4), 119 (30), 117 (46), 105 (4), 91 (3), 71 (5), 39 (2). − ***exo*-13a:** t_R = 12.16 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.54 (s, 9 H, CMe$_3$), 1.57 (dm, $J_{7a,7s}$ = 8.7 Hz, 1 H, H-7$_a$), 2.63 (dm, $J_{7s,7a}$ = 8.7 Hz, 1 H, H-7$_s$), 3.04 (d, *J* = 11.1 Hz, 1 H, CH$_2$), 3.24 (s, 3 H, CH$_3$), 3.32 (s, 1 H, H-1), 3.61 (s, 1 H, H-4), 4.03 (d, *J* = 11.1 Hz, 1 H, CH$_2$), 5.26 (s, 1 H, 8-H$_{a/s}$), 5.30 (s, 1 H, 8-H$_{a/s}$), 6.19 (dd, $J_{5,6}$ = 5.4, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 6.25 (dd, $J_{6,5}$ = 5.4, $J_{6,1}$ = 3.0 Hz, 1 H, 6-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 25.23 (C*Me*$_3$), 46.59 (C-7), 48.85 (C-1/4), 50.79 (C-1/4), 57.93 (CH$_3$), 67.70 (*C*Me$_3$), 75.89 (CH$_2$), 80.20 (C-2), 111.55

(C-8), 135.72 (C-5/6), 138.82 (C-5/6), 146.68 (C-3). − GC MS: *m*/*z* (%) = 270 [M$^+$] (1), 187 (1), 149 (100), 135 (2), 119 (6), 117 (24), 105 (1), 91 (1), 71 (1), 39 (1). − **14a:** t_R = 12.42 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.31 (s, 9 H, CMe$_3$), 2.05 (dm, $J_{7,7}$ = 6.7 Hz, 1 H, 7-H), 2.24 (dm, $J_{7,7}$ = 6.7 Hz, 1 H, 7-H), 2.93 (t, $J_{8,9}$ = 6.4 Hz, 2 H, 8-H), 3.33 (s, 3 H, CH$_3$), 3.54 (t, $J_{9,8}$ = 6.4 Hz, 2 H, CH$_2$), 3.75 (s, 1 H, 4-H), 3.92 (s, 1 H, 1-H), 6.78 (dd, $J_{6,5}$ = 5.0, $J_{6,1}$ = 3.4 Hz, 1 H, 6-H), 6.94 (dd, $J_{5,6}$ = 5.0, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.22 (C*Me*$_3$), 30.12 (C-8), 54.29 (C-1/4), 56.98 (C-1/4), 58.55 (CH$_3$), 60.03 (*C*Me$_3$), 70.57 (C-7), 72.43 (CH$_2$), 141.28 (C-5/6), 143.20 (C-3), 143.46 (C-5/6), 173.35 (C-2). − GC MS: *m/z* (%) = 271 [M$^+$ + 1] (100), 255 (2), 215 (4), 197 (15), 165 (33), 152 (12), 135 (68), 115 (10), 104 (15), 91 (5), 71 (20), 39 (7). − ***endo*-13a/*exo*-13a/14a:** C$_{14}$H$_{22}$O$_3$S (270.4): calcd. C 62.19, H 8.20; found C 62.18, H 8.32.

***endo*- and *exo*-2-Deuterio-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-13b and *exo*-13b) and 3-Deuteriomethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hepta-2,5-diene (14b):** CF$_3$COOD (1.15 mL, 2 m in THF, 2.3 mmol) was added to the solution of **3** at −78 °C or −105 °C after t_{isn}. Workup gave a mixture of *endo*-**13b**, *exo*-**13b**, and **14b** as a colorless solid. − ***endo*-13b:** t_R = 10.80 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.47 (s, 9 H, CMe$_3$), 1.55 (dm, $J_{7s,7a}$ = 8.7 Hz, 1 H, 7-H$_s$), 1.70 (dm, $J_{7a,7s}$ = 8.7 Hz, 1 H, 7-H$_a$), 3.33 (sm, 2 H, 1-H, 4-H), 5.28 (s, 1 H, 8-H$_{a/s}$), 5.29 (s, 1 H, 8-H$_{a/s}$), 6.29 (st, 2 H, 5-H, 6-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.82 (C*Me*$_3$), 46.81 (C-1), 49.79 (C-7), 51.95 (C-4), 60.32 (*C*Me$_3$), 110.44 (C-8), 134.01 (C-6), 135.32 (C-5), 144.14 (C-3). − GC MS: *m/z* (%) = 228 [M$^+$ + 1] (10), 212 (2), 198 (2), 172 (100), 162 (4), 138 (2), 123 (6), 106 (79), 92 (3), 80 (2), 65 (2), 57 (10), 41 (9), 39 (9). − ***exo*-13b:** t_R = 10.61 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.48 (s, 9 H, CMe$_3$), 1.70 (dm, $J_{7a,7s}$ = 9.1 Hz, 1 H, 7-H$_a$), 2.09 (dm, $J_{7s,7a}$ = 9.1 Hz, 1 H, 7-H$_s$), 3.30 (s, 1 H, 1-H), 3.39 (s, 1 H, 4-H), 5.29 (s, 1 H, 8-H$_s$), 5.39 (s, 1 H, 8-H$_a$), 6.18 (dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H), 6.35 (dd, $J_{6,5}$ = 5.7, $J_{6,1}$ = 3.0 Hz, 1 H, 6-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.07 (C*Me*$_3$), 47.50 (C-1), 48.19 (C-7), 49.65 (C-4), 61.05 (*C*Me$_3$), 112.45 (C-8), 134.70 (C-6), 140.60 (C-5), 143.03 (C-3). − GC MS: *m/z* (%) = 228 [M$^+$ + 1] (1), 211 (2), 197 (1), 172 (100), 162 (5), 154 (5), 123 (3), 106 (85), 89 (5), 80 (5), 66 (4), 57 (13), 43 (13), 41 (12), 39 (11). − **14b:** t_R = 10.41 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.30 (s, 9 H, CMe$_3$), 2.04 (dm, $J_{7,7}$ = 6.7 Hz, 1 H, 7-H), 2.21 (tm, $J_{8,8}$ = 6.7 Hz, 2 H, 8-H), 2.25 (dm, $J_{7,7}$ = 6.7 Hz, 1 H, 7-H), 3.52 (s, 1 H, 1-H), 3.92 (s, 1 H, 4-H), 6.81 (dd, $J_{6,5}$ = 5.0, $J_{6,1}$ = 3.4 Hz, 1 H, 6-H), 6.96 (dd, $J_{5,6}$ = 5.0, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = −5.38 (C-8), 23.14 (C*Me*$_3$), 54.28 (C-1/4), 58.82 (C-1/4), 72.28 (C-7), 140.52 (C-5/6), 143.84 (C-5/6). − GC MS: *m/z* (%) = 228 [M$^+$ + 1] (2), 172 (4), 154 (4), 123 (4), 106 (18), 89 (27), 61 (11), 57 (12), 43 (100), 32 (38). − ***endo*-13b/*exo*-13b/14b:** C$_{12}$DH$_{17}$O$_2$S (227.3): calcd. C 63.40, H 7.98; found C 63.20, H 8.00.

***endo*- and *exo*-2-Methyl-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-13c and *exo*-13c) and 3-Ethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hepta-2,5-diene (14c):** MeI (0.14 mL, 2.3 mmol) was added to the solution of **3** at −78 °C or −105 °C after t_{isn}. Quenching with CF$_3$COOD after t_{ren} and workup gave a mixture of *endo*-**13c**, *exo*-**13c**, and **14c** as a colorless solid. Pure *exo*-**13c** was isolated by chromatography (*n*-hexane/EtOAc, 2:1) as colorless crystals, m.p. 101−103 °C. − ***endo*-13c:** t_R = 11.64 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.51 (s, 9 H, CMe$_3$), 1.69 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, 7-H), 1.82 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, 7-H), 1.91 (s, 3 H, CH$_3$), 3.13 (s, 1 H, 1-H), 3.28 (s, 1 H, 4-H), 5.23 (s, 1 H, 8-H$_a$), 5.49 (s, 1 H, 8-H$_s$), 6.16 (dd, $J_{6,5}$ = 5.4, $J_{6,1}$ = 3.4 Hz, 1 H, H-6), 6.32 (dd, $J_{5,6}$ = 5.4, $J_{5,4}$ = 3.0 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 25.90 (C*Me*$_3$), 26.86 (CH$_3$), 49.12 (C-7), 51.25 (C-1/4), 52.40 (C-1/4), 65.20 (*C*Me$_3$), 73.63 (C-2), 109.90 (C-8), 135.38 (C-5/6), 135.86 (C-5/6), 151.13 (C-3). − GC MS: *m/z* (%) = 241 [M$^+$ + 1] (1), 223 (1), 209 (1), 185 (40), 167 (2), 157 (2), 119 (63), 105 (3), 91 (17), 89 (100), 79 (2), 66 (2), 61 (26), 57 (6). − ***exo*-13c:** t_R = 11.48 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.56 (s, 9 H, CMe$_3$), 1.58 (dm, $J_{7a,7s}$ = 9.1 Hz, 1 H, 7-H$_a$), 1.60 (s, 3 H, CH$_3$), 2.68 (dm, $J_{7s,7a}$ = 9.1 Hz, 1 H, 7-H$_s$), 3.35 (s, 1 H, 4-H), 3.50 (s, 1 H, 1-H), 5.30 (s, 1 H, 8-H$_a$), 5.34 (s, 1 H, 8-H$_s$), 6.19 (dd, $J_{6,5}$ = 5.4, $J_{6,1}$ = 2.7 Hz, 1 H, 6-H), 6.29 (dd, $J_{5,6}$ = 5.4, $J_{5,4}$ = 3.4 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.02 (CH$_3$), 26.06 (C*Me*$_3$), 47.48 (C-7), 50.51 (C-1), 51.29 (C-4), 66.09 (*C*Me$_3$), 76.33 (C-2), 110.85 (C-8), 135.23 (C-6), 139.79 (C-5), 150.25 (C-3). − GC MS: *m/z* (%) = 241 [M$^+$ + 1] (1), 237 (1), 213 (1), 185 (57), 157 (5), 119 (100), 104 (2), 91 (20), 89 (73), 79 (2), 66 (3), 61 (17), 57 (5). − **14c:** t_R = 11.08 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.06 (t, $J_{9,8}$ = 7.4 Hz, 3 H, CH$_3$), 1.30 (s, 9 H, CMe$_3$), 2.04 (dm, 1 H, 7-H), 2.21 (dm, 1 H, 7-H), 2.68 (m, 2 H, H-8), 3.63 (s, 1 H, 1/4-H), 3.92 (s, 1 H, 1/4-H), 6.77 (dd, 1 H, 5/6-H), 6.95 (dd, 1 H, 5/6-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 10.90 (C-8), 22.98 (CH$_3$), 23.19 (C*Me*$_3$), 54.20 (C-1/4), 56.19 (C-1/4), 72.15 (C-7), 140.91 (C-5/6), 143.64 (C-5/6). − GC MS: *m/z* (%) = 241 [M$^+$ + 1] (1), 185 (6), 167 (2), 119 (10), 105 (1), 91 (5), 89 (100), 79 (1), 70 (2), 66 (2), 61 (23), 57 (2). − ***endo*-13c/*exo*-13c/14c:** C$_{13}$H$_{20}$O$_2$S (240.4): calcd. C 64.96, H 8.39; found C 64.79, H 8.40.

In situ Methylation of 3: *endo*- and *exo*-2-Methyl-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-13c and *exo*-13c) and 3-Ethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo-[2.2.1]hepta-2,5-diene (14c): Neat MeI (0.14 mL, 2.3 mmol) was added at −78 °C (−105 °C) to a solution of *endo*-**9** or *exo*-**9** (52 mg, 0.23 mmol) in THF (5 mL). The solution was subsequently treated dropwise with *n*BuLi (0.16 mL, 1.6 m in *n*-hexane, 0.25 mmol) at this temperature. Stirring of the mixture was continued at −78 °C (−105 °C) for 10 min. Workup gave a mixture of *endo*-**13c**, *exo*-**13c**, and **14c** as a colorless solid.

***endo*- and *exo*-2-Allyl-3-methylene-2-(2-methylpropyl-2-sulfonyl)-bicyclo[2.2.1]hept-5-ene (*endo*-13d and *exo*-13d) and 3-(But-3-enyl)-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hepta-2,5-diene (14d):** Allyl iodide (0.21 mL, 2.3 mmol) was added to the solution of **3** after 1 min at −105 °C. Quenching with CF$_3$COOD after t_{ren} and workup gave a mixture of *endo*-**13d**, *exo*-**13d**, and **14d** as a colorless oil. − ***endo*-13d:** t_R = 12.58 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.52 (s, 9 H, CMe$_3$), 1.46−1.60 (dm, 1 H, 7-H), 1.91 (dm, 1 H, 7-H), 2.76 (m, 2 H, CH$_2$), 3.20 (s, 1 H, 1/4-H), 3.24 (s, 1 H, 1/4-H), 4.94−5.10 (m, 2 H, =CH$_2$), 5.34 (s, 1 H, 8-H$_{a/s}$), 5.42 (s, 1 H, 8-H$_{a/s}$), 5.95−6.15 (m, 1 H, =CH), 6.19 (m, 1 H, 5/6-H), 6.25 (m, 1 H, 5/6-H). − GC MS: *m/z* (%) = 267 [M$^+$ + 1] (43), 211 (44), 153 (8), 145 (65), 131 (6), 117 (9), 105 (8), 91 (11), 89 (100), 75 (5), 61 (46). − ***exo*-13d:** t_R = 12.52 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.55 (s, 9 H, CMe$_3$), 1.59 (dm, $J_{7a,7s}$ = 8.7 Hz, 1 H, 7-H$_a$), 2.62 (dm, $J_{7s,7a}$ = 8.7 Hz, 1 H, 7-H$_s$), 2.73 (dd, J = 16.12, J = 7.4 Hz, 1 H, CH$_2$), 3.36 (s, 1 H, 1/4-H), 3.54 (s, 1 H, 1/4-H), 4.99 (dm, J = 10.1 Hz, 1 H, =CH$_{2cis}$), 5.06 (dm, J = 16.8 Hz, 1 H, =CH$_{2trans}$), 5.25 (s, 1 H, 8-H$_{a/s}$), 5.35 (s, 1 H, 8-H$_{a/s}$), 5.86 (m, 1 H, =CH), 6.19 (dd, $J_{6,5}$ = 5.4, $J_{6,1}$ = 3.0 Hz, 1 H, 6/5-H), 6.25 (dd, $J_{5,6}$ = 5.4, $J_{5,4}$ = 3.0 Hz, 1 H, 5/6-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.33 (C*Me*$_3$), 42.22 (CH$_2$), 47.79 (C-7), 50.42 (C-1/4), 51.70 (C-1/4), 111.74 (C-8), 117.04 (=CH$_2$), 135.60 (=CH), 137.25 (C-5/6), 139.19 (C-5/6). − GC MS: *m/z* (%) = 267 [M$^+$ + 1] (26), 211 (34), 153 (6), 145 (5), 105 (3), 89 (100), 75 (4), 61 (46), 47 (3). − **14d:** t_R = 12.30 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.30 (s, 9 H, CMe$_3$), 2.04 (dm, $J_{7,7}$ = 6.7 Hz, 1 H, 7-

H), 2.22 (dm, $J_{7,7}$ = 6.7 Hz, 1 H, 7-H), 2.23 (m, 2 H, 8-H), 2.76 (m, 2 H, CH$_2$), 3.67 (s, 1 H, 1/4-H), 3.92 (s, 1 H, 1/4-H), 4.99 (dm, $J_{10,11}$ = 10.1 Hz, 1 H, =CH$_{2cis}$), 5.06 (dm, J = 16.8 Hz, 1 H, =CH$_{2trans}$), 5.81 (ddm, J = 16.8, J = 10.1 Hz, 1 H, =CH), 6.77 (dd, $J_{6,5}$ = 5.0, $J_{6,1}$ = 3.0 Hz, 1 H, 6/5-H), 6.95 (dd, $J_{5,6}$ = 5.0, $J_{5,4}$ = 3.4 Hz, 1 H, 5/6-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.26 (C*Me*$_3$), 29.17 (C-8), 31.21 (CH$_2$), 54.31 (C-1/4), 56.40 (C-1/4), 60.01 (*C*Me$_3$), 72.26 (C-7), 115.55 (=CH$_2$), 135.34 (=CH), 140.91 (C-5/6), 143.65 (C-5/6), 174.83 (C-3). − GC MS: *m*/*z* (%) = 267 [M$^+$ + 1] (100), 211 (88), 193 (56), 183 (7), 163 (38), 145 (56), 131 (5), 117 (5), 89 (6). − ***endo*-13d/*exo*-13d/14d:** C$_{15}$H$_{22}$O$_2$S (266.4): calcd. C 67.63, H 8.32; found C 67.43, H 8.46.

***endo*- and *exo*-Benzhydrylidene-2-methoxymethyl-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-15a and *exo*-15a and Benzhydrylidene-3-methoxyethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hepta-2,5-diene (16a):** *n*BuLi (0.14 mL, of 1.60 m in *n*-hexane, 0.22 mmol) was added dropwise at −105 °C to a solution of *endo*-**10**/*exo*-**10** (2.6:1) (78 mg, 0.20 mmol) in THF (5 mL). After the solution had been stirred at the given temperature for t_{isn}, MeOCH$_2$I (0.17 mL, 2.0 mmol) was added. After the solution had been stirred at −105 °C for 10 min, CF$_3$COOD (1.0 mL of 2 m in THF, 2.0 mmol) was added and stirring at this temperature was continued for 10 min. The usual workup afforded a mixture of *endo*-**15a**, *exo*-**15a**, and **16a** as a yellow oil. − ***endo*-15a:** R_f = 0.43 (cyclohexane/EtOAc, 2:1). − t_R = 24.16 min (permethyl-β-cyclodextrin). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.42 (s, 9 H, CMe$_3$), 2.88 (s, 3 H, 11-H), 3.84 (br. s, 1 H, 4-H), 4.18 (br. s, 1 H, 1-H), 4.20 (d, $J_{10,10}$ = 11.1 Hz, 1 H, 10-H), 4.62 (d, $J_{10,10}$ = 11.1 Hz, 1 H, 10-H), 5.36 (s, 1 H, 8-H$_a$), 5.59 (s, 1 H, 8-H$_s$), 6.44 (m, 2 H, 5-H, 6-H), 7.05−7.35 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.50 (C*Me*$_3$), 49.74 (C-1/4), 54.00 (C-1/4), 57.45 (C-11), 67.11 (*C*Me$_3$), 70.40 (C-2), 74.95 (C-10), 111.00 (C-8), 124.14 (C-7), 126.92 and 127.02 (*p*-C), 127.82, 128.10, 129.26 and 129.47 (*o*-, *m*-C), 133.59 (C-5/6), 136.81 (C-5/6), 140.10 and 140.72 (*i*-C), 145.08 (C-9), 148.50 (C-3). − ***exo*-15a:** R_f = 0.48 (cyclohexane/EtOAc, 2:1). − t_R = 24.09 min (permethyl-β-cyclodextrin). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.08 (s, 9 H, CMe$_3$), 3.19 (d, $J_{10,10}$ = 10.7 Hz, 1 H, 10-H), 3.24 (s, 3 H, 11-H), 3.81 (br. s, 1 H, 1-H), 4.06 (d, $J_{10,10}$ = 10.7 Hz, 1 H, 10-H), 4.15 (br. s, 1 H, 4-H), 5.36 (s, 1 H, 8-H$_a$), 5.47 (s, 1 H, 8-H$_s$), 6.44 (m, 2 H, 5-H, 6-H), 7.10−7.32 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.54 (C*Me*$_3$), 49.90 (C-1/4), 53.49 (C-1/4), 57.93 (C-11), 67.66 (*C*Me$_3$), 74.67 (C-10), 79.68 (C-2), 112.01 (C-8), 124.59 (C-7), 126.56 and 126.58 (*p*-C), 127.62, 127.92, 129.93 and 130.07 (*o*-, *m*-C), 134.47 (C-5/6), 140.52 (C-5/6), 141.17 and 141.51 (*i*-C), 144.00 (C-9), 148.31 (C-3). − **16a:** R_f = 0.36 (cyclohexane/EtOAc, 2:1). − t_R = 24.14 min (permethyl-β-cyclodextrin). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.21 (s, 9 H, CMe$_3$), 3.02 (m, 2 H, 8-H), 3.25 (s, 3 H, 11-H), 3.53 (m, 2 H, 10-H), 4.27 (tm, 1 H, 1-H/4-H), 4.46 (tm, 1 H, 1-H/4-H), 6.95 (m, 2 H, 5-H, 6-H), 7.05−7.35 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 22.98 (C*Me*$_3$). − ***endo*-15a/*exo*-15a/16a:** GC MS: *m*/*z* (%) = 434 [M$^+$] (100), 402 (44), 377 (8), 361 (24), 330 (31), 314 (37), 300 (9), 282 (62), 266 (50), 254 (34), 240 (12), 216 (8), 203 (21), 189 (9), 165 (8), 139 (2), 105 (3), 71 (1), 45 (5).

***endo*- and *exo*-Benzhydrylidene-2-deuterio-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-5-ene (*endo*-15b and *exo*-15b) and Benzhydrylidene-3-deuteriomethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hepta-2,5-diene (16b):** *n*BuLi (0.14 mL of 1.60 m in *n*-hexane, 0.22 mmol) was added dropwise at −105 °C to a solution of *endo*-10/*exo*-10 (3:1) (78 mg, 0.20 mmol) in THF (5 mL). After the yellow mixture had been stirred at the given temperature for t_{isn}, CF$_3$COOD (1.0 mL of 2 m in THF, 2.0 mmol) was added and stirring was continued at this temperature for 10 min. The usual workup afforded a mixture of *endo*-**15b**, *exo*-**15b**, and **16b** as a colorless solid. R_f (*endo*-**15b**/*exo*-**15b**/**16b**) = 0.40 (cyclohexane/EtOAc, 2:1). − *endo*-**15b**: t_R = 11.37 min (permethyl-β-cyclodextrin). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.43 (s, 9 H, CMe$_3$), 3.82 (br. s, 1 H, 1-H), 3.89 (br. s, 1 H, 4-H), 5.34 (br. s, 2 H, 8-H$_{a/s}$), 6.52 (sm, 2 H, 5-H,6-H), 7.05−7.35 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.74 (C*Me*$_3$), 49.05 (C-1/4), 53.96 (C-1/4), 60.44 (*C*Me$_3$), 61.34 (C-2), 110.83 (C-8), 123.71 (C-7), 127.13 and 127.22 (*p*-C), 128.07, 128.17, 129.44 and 129.60 (*o*-, *m*-C), 134.36 (C-5/6), 135.76 (C-5/6), 140.21 and 140.27 (*i*-C), 142.19 (C-9), 148.77 (C-3). − GC MS: *m*/*z* (%) = 391 [M$^+$] (53), 336 (41), 327 (49), 318 (98), 301 (9), 285 (11), 271 (100), 255 (39), 229 (13), 215 (8), 192 (15), 130 (5), 89 (63), 61 (6). − *exo*-**15b**: t_R = 11.53 min (permethyl-β-cyclodextrin). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.18 (s, 9 H, CMe$_3$), 3.79 (br. s, 1 H, 1-H), 3.96 (br. s, 1 H, 4-H), 5.47 (s, 1 H, 8-H$_a$), 5.55 (s, 1 H, 8-H$_s$), 6.44 (dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 3.4 Hz, 1 H, 5-H), 6.54 (dd, $J_{6,5}$ = 5.7, $J_{6,1}$ = 3.0 Hz, 1 H, 6-H), 7.05−7.35 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.22 (C*Me*$_3$), 47.57 (C-1/4), 52.91 (C-1/4), 61.39 (*C*Me$_3$), 62.96 (C-2), 112.22 (C-8), 126.40 (C-7), 126.79 and 126.88 (*p*-C), 127.75, 127.98, 129.84 and 129.96 (*o*-, *m*-C), 133.70 (C-5/6), 139.80 (C-9), 140.77 and 141.14 (*i*-C), 142.10 (C-5/6), 147.66 (C-3). − GC MS: *m*/*z* (%) = 391 [M$^+$] (64), 336 (34), 327 (32), 318 (100), 300 (22), 285 (8), 271 (87), 255 (43), 239 (13), 229 (13), 215 (8), 192 (15), 130 (5). − **16b**: t_R = 11.29 min (β-CD). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.21 (s, 9 H, CMe$_3$), 2.30 (tm, 2 H, 8-H), 4.02 (tm, 1 H, 1/4-H), 4.48 (tm, 1 H, 1/4-H), 6.96−7.04 (m, 2 H, 5-H, 6-H), 7.05−7.35 (m, 10 H, *o*-, *m*-, *p*-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = −5.45 (C-8), 22.99 (C*Me*$_3$), 55.35 (C-1/4), 60.02 (C-1/4), 60.51 (*C*Me$_3$), 67.95 (C-7), 99.40 (C-9), 126.84 (*p*-C), 128.12 and 129.66 (*o*-, *m*-C), 139.06 (C-3), 139.36 (*i*-C), 140.65 (C-5/6), 143.07 (C-5/6), 163.21 (C-2). − GC MS: *m*/*z* (%) = 391 [M$^+$] (72), 336 (26), 327 (30), 318 (100), 300 (21), 285 (9), 270 (88), 255 (52), 239 (13), 229 (15), 215 (9), 192 (14), 130 (3). − ***endo*-15b/*exo*-15b/16b**: C$_{25}$DH$_{25}$O$_2$S (391.5): calcd. C 76.69, H 6.95; found C 76.57, H 7.11.

***endo*- and *exo*-2-Deuterio-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]heptane (*endo*-17a and *exo*-17a) and 3-Deuteriomethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-2-ene (18a):** *n*BuLi (0.16 mL of 1.60 m in *n*-hexane, 0.25 mmol) was added dropwise at −78 °C to a solution of *endo*-**12** or *exo*-**12** (52.5 mg, 0.23 mmol) in THF (5 mL). After the solution had been stirred at this temperature for 30 min, CF$_3$COOD (1.15 mL of 2 m in THF, 2.3 mmol) was added and the stirring was continued at −78 °C for 10 min. The usual workup afforded a mixture of *endo*-**17a**, *exo*-**17a**, and **18a** (47 mg, 95%) in a ratio of 5:54:41 (GC) and a mixture of *endo*-**17a**, *exo*-**17a** and **18a** (50 mg, 95%) in a ratio of 6:49:45 (GC), respectively, as colorless oils. R_f (*endo*-**17a**/*exo*-**17a**/**18a**) = 0.37 (*n*-hexane/EtOAc, 2:1). − ***endo*-17a:** t_R = 11.13 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.46 (s, 9 H, CMe$_3$), 1.48 (sm, 3 H, 6-H$_{exo}$/7-H$_a$/7-H$_s$), 1.57 (m, 1 H, 5-H), 1.72 (m, 1 H, 5-H), 2.35 (m, 1 H, 6-H$_{endo}$), 2.80 (br. s, 1 H, 4-H), 2.85 (sd, 1 H, 1-H), 5.19 (s, 1 H, 8-H$_a$), 5.42 (s, 1 H, 8-H$_s$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 22.83 (C-6), 24.01 (C*Me*$_3$), 28.37 (C-5), 39.65 (C-7), 41.33 (C-1), 46.40 (C-4), 60.97 (*C*Me$_3$), 109.45 (C-8), 146.10 (C-3). − GC MS: *m*/*z* (%) = 230 [M$^+$ + 1] (3), 215 (2), 189 (1), 174 (93), 165 (5), 150 (6), 137 (3), 108 (72), 89 (45), 81 (59), 57 (78), 43 (100), 41 (65), 39 (42), 32 (33). − ***exo*-17a:** t_R = 11.08 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.30 (m, 1 H, 6-H$_{endo}$), 1.34 (dm, $J_{7a,7s}$ = 10.1 Hz, 1 H, 7-H$_a$), 1.40 (m, 1 H, 5-H$_{endo}$), 1.46 (s, 9 H, CMe$_3$), 1.72 (m, 2 H, 5-H$_{exo}$/6-H$_{exo}$), 2.00 (dm, $J_{7s,7a}$ = 10.1 Hz, 1 H, 7-H$_s$), 2.82 (br. s, 1 H, 1-H), 2.87 (br. s, 1 H, 4-H), 5.22 (s, 1 H, 8-

H$_a$), 5.33 (s, 1 H, 8-H$_s$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.07 (C*Me*$_3$), 27.30 (C-6), 30.15 (C-5), 37.50 (C-7), 42.10 (C-1), 44.20 (C-4), 60.78 (*C*Me$_3$), 111.72 (C-8), 146.81 (C-3). − GC MS: *m*/*z* (%) = 230 [M$^+$ + 1] (1), 215 (5), 189 (2), 174 (100), 156 (3), 137 (2), 108 (46), 89 (2), 81 (10), 57 (8), 43 (6), 41 (9), 39 (8), 32 (2). − **18a:** t_R = 10.73 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.20 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, 7-H), 1.20−1.30 (m, 2 H, 6-H), 1.36 (s, 9 H, CMe$_3$), 1.50−1.60 (m, 2 H, 5-H), 1.81 (dm, $J_{7,7}$ = 8.7 Hz, 1 H, 7-H), 2.10 (tm, $J_{8,4}$ = 2.3 Hz, 2 H, 8-H), 2.87 (br. s, 1 H, 1-H), 3.23 (br. s, 1 H, 4-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.12 (C*Me*$_3$), 46.40 (C-8), 47.00 (C-1/4), 51.13 (C-1/4), 69.72 (*C*Me$_3$), 134.09 (C-2/3), 162.90 (C-2/3). − GC MS: *m*/*z* (%) = 230 [M$^+$ + 1] (25), 174 (12), 156 (100), 128 (11), 108 (12), 89 (5), 81 (15), 57 (15), 43 (15), 41 (15), 39 (20), 32 (5). − ***endo*-17a/*exo*-17a/18a:** C$_{12}$DH$_{19}$O$_2$S (229.3): calcd. C 62.84, H 8.79; found C 62.56, H 8.74.

***exo*-2-Methyl-3-methylene-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]heptane (*exo*-17b) and 3-Ethyl-2-(2-methylpropyl-2-sulfonyl)bicyclo[2.2.1]hept-2-ene (18b). − Stepwise Reaction:** *n*BuLi (0.16 mL of 1.60 m in *n*-hexane, 0.25 mmol) was added dropwise at −78 °C to a solution of *endo*-**12** or *exo*-**12** (52.5 mg, 0.23 mmol) in THF (5 mL). After the colorless solution had been stirred at this temperature for 30 min, MeI (0.14 mL, 2.3 mmol) was added dropwise. The usual workup afforded a mixture of *exo*-**17b** and **18b** (50 mg, 90%) in a ratio of 15:85 (GC) or a mixture of *exo*-**17b** and **18b** (50 mg, 90%) in a ratio of 14:86 (GC), respectively, as colorless oils. − ***exo*-17b:** R_f = 0.41 (*n*-hexane/EtOAc, 2:1). − t_R = 11.93 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.54 (s, 9 H, CMe$_3$), 1.72 (s, 3 H, 9-H), 1.20−1.80 (m, 5 H, 7-H$_a$, 5-H, 6-H), 2.83 (sm, 2 H, 1-H, 7-H$_s$), 2.94 (br. s, 1 H, 4-H), 5.18 (s, 1 H, 8-H$_{a/s}$), 5.28 (s, 1 H, 8-H$_{a/s}$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.42 (C-9), 25.24 (C-5/6), 26.18 (C*Me*$_3$), 29.93 (C-5/6), 37.21 (C-7), 45.02 (C-1/4), 45.89 (C-1/4), 66.04 (*C*Me$_3$), 108.97 (C-8), 155.23 (C-3). − GC MS: *m*/*z* (%) = 243 [M$^+$ + 1] (1), 187 (2), 169 (12), 141 (3), 121 (2), 89 (18), 79 (3), 70 (3), 61 (11), 57 (7), 43 (100), 32 (45). − **18b:** R_f = 0.47 (*n*-hexane/EtOAc, 2:1). − t_R = 11.43 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.12 (t, $J_{9,8}$ = 7.7 Hz, 3 H, 9-H), 1.23 (dm, $J_{7,7}$ = 8.4 Hz, 1 H, 7-H), 1.36 (s, 9 H, CMe$_3$), 1.81 (dm, $J_{7,7}$ = 8.4 Hz, 1 H, 7-H), 1.20−1.80 (m, 4 H, 5-H, 6-H), 2.54 (dq, $J_{8,8}$ = 15.1, $J_{8,9}$ = 7.7 Hz, 1 H, 8-H), 2.68 (dq, $J_{8,8}$ = 15.1, $J_{8,9}$ = 7.7 Hz, 1 H, 8-H), 3.06 (sm, 1 H, 1-H/4-H), 3.24 (br. s, 1 H, 1-H/4-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.35 (C-9), 21.36 (C-5/6), 23.19 (C*Me*$_3$), 24.54 (C-5/6), 26.92 (C-7), 46.85 (C-8), 47.01 (C-1/4), 48.07 (C-1/4), 59.46 (*C*Me$_3$), 133.38 (C-3), 167.93 (C-2). − GC MS: *m*/*z* (%) = 243 [M$^+$ + 1] (4), 187 (10), 169 (100), 151 (8), 141 (18), 121 (3), 109 (4), 91 (8), 89 (7), 79 (4), 65 (4), 57 (19), 43 (28), 32 (11). − ***exo*-17b/18b:** C$_{13}$H$_{22}$O$_2$S (242.3): calcd. C 64.42, H 9.15; found C 64.20, H 9.11. − **In situ Reaction:** *n*BuLi (0.16 mL of 1.60 m in *n*-hexane, 0.25 mmol) was added dropwise at −78 °C to a solution of *endo*-**12** or *exo*-**12** (52.5 mg, 0.23 mmol) and MeI (0.14 mL, 2.3 mmol) in THF (5 mL). The usual workup afforded a mixture of *exo*-**17b** and **18b** (53 mg, 95%) in a ratio of 14:86 (GC) or a mixture of *endo*-**17b**, *exo*-**17b**, and **18b** (52 mg, 93%) in a ratio of 5:29:66 (GC), respectively, as colorless solids.

***endo*- and *exo*-2-Deuterio-3-methylene-2-(2-methylpropyl-2-sulfonyl)-7-oxabicyclo[2.2.1]hept-5-ene (*endo*-19 and *exo*-19):** *n*BuLi (0.16 mL of 1.60 m in *n*-hexane, 0.25 mmol) was added dropwise at −105 °C to a solution of *endo*-**11** or *endo*-**11**/*exo*-**11** (2:1) (52.5 mg, 0.23 mmol) in THF (5 mL). After the mixture had been stirred at this temperature for t_{isn}, CF$_3$COOD (1.15 mL of 2 m in THF, 2.3 mmol) was added and stirring at this temperature was continued for 10 min. The usual workup furnished a mixture of *endo*-**19**, *exo*-**19**, and the rearrangement product as a colorless solid. − ***endo*-19:** R_f = 0.34 (*n*-hexane/EtOAc, 1:1). − t_R = 10.75 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.47 (s, 9 H, CMe$_3$), 5.14 (br. s, 1 H, 4-H), 5.24 (br. s, 1 H, 1-H), 5.36 (s, 1 H, 8-H$_{a,s}$), 5.37 (s, 1 H, 8-H$_{a,s}$), 6.57 (dd, $J_{6,5}$ = 5.8, $J_{6,1}$ = 1.5 Hz, 1 H, 6-H), 6.62 (dd, $J_{5,6}$ = 5.8, $J_{5,4}$ = 1.8 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 23.48 (C*Me*$_3$), 60.20 (*C*Me$_3$), 80.18 (C-1/4), 83.81 (C-1/4), 110.78 (C-8), 133.98 (C-5/6), 135.30 (C-5/6), 139.57 (C-3). − GC MS: *m*/*z* (%) = 230 [M$^+$ + 1] (1), 162 (2), 105 (2), 88 (100), 74 (3), 60 (11), 47 (2). − ***exo*-19:** R_f = 0.28 (*n*-hexane/EtOAc, 1:1). − t_R = 11.03 min (*S2*). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.48 (s, 9 H, CMe$_3$), 5.20 (br. s, 1 H, 4-H), 5.43 (s, 1 H, 1-H), 5.47 (br. s, 1 H, 8-H$_a$), 5.55 (br. s, 1 H, 8-H$_s$), 6.43 (dd, $J_{6,5}$ = 5.5, $J_{6,1}$ = 1.8 Hz, 1 H, 6-H), 6.59 (dd, $J_{5,6}$ = 5.5, $J_{5,4}$ = 1.5 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.22 (C*Me*$_3$), 63.33 (*C*Me$_3$), 81.10 (C-1/4), 81.81 (C-1/4), 112.31 (C-8), 134.20 (C-5/6), 137.80 (C-3), 138.16 (C-5/6). − GC MS: *m*/*z* (%) = 230 [M$^+$ + 1] (1), 173 (13), 161 (3), 155 (6), 109 (79), 91 (32), 88 (100), 81 (2), 68 (2), 60 (11), 47 (2). − ***endo*-19/*exo*-19:** C$_{11}$DH$_{15}$O$_3$S (229.3): calcd. C 57.61, H 7.03; found C 57.42, H 7.07.

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This mechanism is different from stepwise H/D-exchange through successive treatment of the sulfone with *n*BuLi and CF_3COOD, since no formation of the free anion occurs (see ref. [7]). This is also indicated by the high α,γ-regioselectivity of the H/D-exchange.

[36] A high-yield methylation and allylation of the *S*-phenyl analog of **11** at the 2-position has been achieved by deprotonation and treatment with electrophiles at −100 °C: M. van Gumpel, PhD Thesis, RWTH Aachen, **1999**.

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