Lithiated Compounds

Chiral Lithiated Allylic α-Sulfonyl Carbanions: Experimental and Computational Study of Their Structure, Configurational Stability, and Enantioselective Synthesis

Frank Gerhards,[a, b] Nicole Griebel,[a, c] Jan Runsink†,[a] Gerhard Raabe,*[a] and Hans-Joachim Gais*[a]

Abstract: X-ray crystal structure analysis of the lithiated allylic α-sulfonyl carbanions $[CH_2{=}CHC(Me)SO_2Ph]Li\cdot diglyme$, $[cC_6H_8SO_2tBu]Li\cdot PMDETA$ and $[cC_7H_{10}SO_2tBu]Li\cdot PMDETA$ showed dimeric and monomeric CIPs, having nearly planar anionic C atoms, only O–Li bonds, almost planar allylic units with strong C–C bond length alternation and the *s-trans* conformation around C1–C2. They adopt a C1–S conformation, which is similar to the one generally found for alkyl and aryl substituted α-sulfonyl carbanions. Cryoscopy of $[EtCH{=}CHC(Et)SO_2tBu]Li$ in THF at 164 K revealed an equilibrium between monomers and dimers in a ratio of 83:17, which is similar to the one found by low temperature NMR spectroscopy. According to NMR spectroscopy the lone-pair orbital at C1 strongly interacts with the C=C double bond. Low temperature ^{6}Li,^{1}H NOE experiments of $[EtCH{=}CHC(Et)SO_2tBu]Li$ in THF point to an equilibrium between monomeric CIPs having only O–Li bonds and CIPs having both O–Li and C1–Li bonds. Ab initio calculation of $[MeCH{=}CHC(Me)SO_2Me]Li\cdot(Me_2O)_2$ gave three isomeric CIPs having the *s-trans* conformation and three isomeric CIPs having the *s-cis* conformation around the C1–C2 bond. All *s-trans* isomers are more stable than the *s-cis* isomers. At all levels of theory the *s-trans* isomer having O–Li and C1–Li bonds is the most stable one followed by the isomer which has two O–Li bonds. The allylic unit of the C,O,Li isomer shows strong bond length alternation and the C1 atom is in contrast to the O,Li isomer significantly pyramidalized. According to NBO analysis of the *s-trans* and *s-cis* isomers, the interaction of the lone pair at C1 with the π^* orbital of the CC double bond is energetically much more favorable than that with the "empty" orbitals at the Li atom. The C1–S and C1–C2 conformations are determined by the stereoelectronic effects n_C–σ_{SR}^* interaction and allylic conjugation. ^{1}H DNMR spectroscopy of racemic $[EtCH{=}CHC(Et)SO_2tBu]Li$, $[iPrCH{=}CHC(iPr)SO_2tBu]Li$ and $[EtCH{=}C(Me)C(Et)SO_2tBu]Li$ in [D$_8$]THF gave estimated barriers of enantiomerization of $\Delta G^{\neq} = 13.2\ kcal\,mol^{-1}$ (270 K), $14.2\ kcal\,mol^{-1}$ (291 K) and $14.2\ kcal\,mol^{-1}$ (295 K), respectively. Deprotonation of sulfone (*R*)-$EtCH{=}CHCH(Et)SO_2tBu$ (94 % *ee*) with *n*BuLi in THF at −105 °C occurred with a calculated enantioselectivity of 93 % *ee* and gave carbanion (*M*)-$[EtCH{=}CHC(Et)SO_2tBu]Li$, the deuteration and alkylation of which with CF_3CO_2D and $MeOCH_2I$, respectively, proceeded with high enantioselectivities. Time-dependent deuteration of the enantioenriched carbanion (*M*)-$[EtCH{=}CHC(Et)SO_2tBu]Li$ in THF gave a racemization barrier of $\Delta G^{\neq} = 12.5\ kcal\,mol^{-1}$ (168 K), which translates to a calculated half-time of racemization of $t_{1/2} = 12$ min at −105 °C.

Introduction

Lithiated allylic α-sulfonyl carbanions **I** and **II** (Figure 1) have found extensive application in organic synthesis.[1–3] This is mainly due to their highly selective reactions with a wide range of electrophiles at the α-position and the exceptional nucleofugacity of the allylic sulfonyl group in, for example, transition metal-mediated reactions with nucleophiles.[4] In stark contrast stands the almost complete neglect of the aspects associated with the chirality of **I**[5] and **II**, including their enantioselective synthesis and configurational stability.[6,7] In addition, knowledge of the structure of **I** and **II** is, with the exception of some particular lithiated bicyclic allylic α-sulfonyl carbanions,[8,9] rather limited.[5,10–13] It was found that chiral dialkyl and alkyl-aryl substituted α-sulfonyl carbanions **IIIa** and **IIIb**, which carry a *S-tert*-butyl and *S*-trifluoromethyl, are config-

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[a] Dr. F. Gerhards, Dr. N. Griebel, Dr. J. Runsink, Prof. Dr. G. Raabe, Prof. Dr. H.-J. Gais
Institute of Organic Chemistry, RWTH Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: gais@rwth-aachen.de

[b] Dr. F. Gerhards
Present address: Philipp Reis Strasse 12
40215 Düsseldorf (Germany)

[c] Dr. N. Griebel
Present address: Kaiserstrasse 66
52080 Aachen (Germany)

[†] Deceased, 2012.

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urationally stable at low temperatures.[7,14–20] They are available through deprotonation of the corresponding chiral *S*-*tert*-butyl and *S*-trifluoromethyl sulfones with organolithiums.[7,14–17,19,20] We became therefore interested in a study of the configurational stability, enantioselective synthesis and structure of the *S*-*tert*-butyl and *S*-trifluoromethyl substituted allylic carbanions **I** and **II** ($R = R^3 = t$Bu, CF_3). Provided **I** and **II** are accessible in enantioenriched and configurationally stable form, they will constitute a new class of chiral heteroatom-stabilized allyllithiums,[1d,21,22] which could have a considerable synthetic potential. We decided to first examine the acyclic and cyclic *S*-*tert*-butyl substituted lithiated allylic carbanions **I** and **II**, respectively. The corresponding chiral acyclic and cyclic allylic *S*-*tert*-butyl sulfones **IV** and **V**, respectively, which are required as starting material for the synthesis of **I** and **II**, can be readily obtained by two different palladium catalyzed enantioselective reactions, allylic alkylation of *tert*-butyl sulfinate with racemic allylic carbonates[23–26] and rearrangement of racemic allylic *S*-*tert*-butylsulfinates.[27–29]

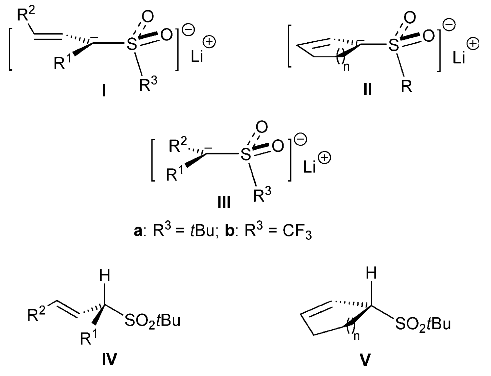


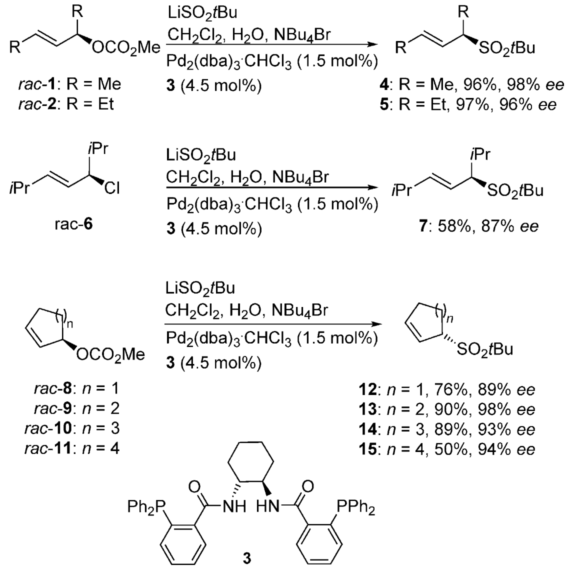
Figure 1. Chiral lithiated allylic and non-allylic α-sulfonyl carbanions.

Herein we describe the enantioselective synthesis, configurational stability, reactivity, and experimental as well as theoretical structures of lithiated allylic α-sulfonyl carbanions.[30]

Results and Discussion

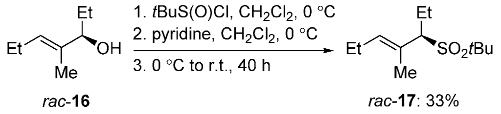
Synthesis of enantiomerically enriched and racemic allylic *tert*-butyl sulfones

As described previously, the (*R*)-configured acyclic allylic *tert*-butyl sulfones **4** and **5** and the (*S*)-configured cyclic allylic *tert*-butyl sulfones **12**–**15** were synthesized through palladium catalyzed alkylation of $LiSO_2t$Bu with the corresponding racemic allylic carbonates *rac*-**1**, *rac*-**2** and *rac*-**8**-**11** in the presence of the chiral bisphosphane **3** in yields of 50 to 98% with 89 to 98% *ee* (Scheme 1).[24–26]



Scheme 1. Palladium catalyzed enantioselective synthesis of allylic *tert*-butyl sulfones.[24–26]

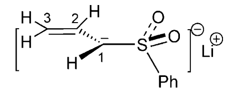
The isopropyl-substituted allylic *tert*-butyl sulfone **7** was prepared starting from the racemic allylic chloride *rac*-**6** and $LiSO_2t$Bu through palladium catalysis in the presence of **3** following the published protocol in 58% yield with 87% *ee*.[25] The corresponding racemic allylic sulfones were either synthesized through palladium catalyzed substitution of the corresponding racemic allylic carbonates and chloride with the sulfinate in the presence of PPh_3 or through racemization of the allylic sulfones via deprotonation–protonation sequences at ambient temperatures. A palladium-catalyzed substitution of the racemic allylic carbonate derived from the racemic allylic alcohol *rac*-**16** with the sulfinate could not be achieved by using **3** or PPh_3 as ligands. Therefore, alcohol *rac*-**16** was treated with racemic *tert*-butylsulfinyl chloride, which directly afforded via the intermediate formation of the corresponding sulfinate and its thermal sulfinate-sulfone rearrangement[31] the racemic allylic *tert*-butyl sulfone *rac*-**17** albeit only in 33% yield (Scheme 2).



Scheme 2. Synthesis of the racemic allylic *tert*-butyl sulfone *rac*-**17**.

Structure in the crystal phase

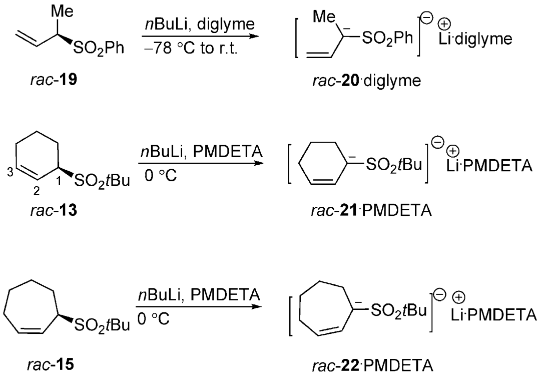
Little information was available about the structure of lithiated acyclic allylic α-sulfonyl carbanions in the crystal. We had previously determined the structure of the lithiated acyclic carbanion *rac*-**18**·diglyme, which crystallized from diglyme (diglyme = diethylene glycol dimethyl ether) as a centro-symmetric diglyme-coordinated dimer that has only O–Li bonds.[5] The anionic C1 atom of *rac*-**18**·diglyme seems to be pyramidalized as indicated by the dihedral angle C2-C1-S-Ci of 76°. However, the uncertainties associated with the determination of the position of the H atom at C1 did not allow a conclusion as to the coordination geometry of the anionic C atom of allylic α-sulfonyl carbanions. The C2–C3 unit of *rac*-**18**·diglyme is nearly in one plane with the C1–S unit as shown by the dihedral angle S-C1-



rac-**18**

C2-C3 of 169° and the carbanion adopts the *s-trans* conformation around the C1–C2 bond.

In order to obtain information about the structure of the more relevant lithiated acyclic allylic α-sulfonyl carbanions carrying an alkyl group at C1, we determined in extension of the study of *rac*-**18**·diglyme the crystal structure of the lithiated methyl substituted carbanion *rac*-**20**. Single crystals of *rac*-**20**·diglyme were obtained from sulfone *rac*-**19** through treatment with *n*BuLi in diglyme and recrystallization of the lithiated carbanion from diglyme (Scheme 3).[10d] The lithiated carbanion *rac*-**20**·diglyme is stable at room temperature under the exclusion of water and dioxygen.



Scheme 3. Synthesis of the lithiated allylic α-sulfonyl carbanions *rac*-**20**·diglyme, *rac*-**21**·PMDETA and *rac*-**22**·PMDETA.

The lithiated carbanion *rac*-**20**·diglyme is also a centro-symmetric diglyme-coordinated dimer, which has O–Li but no C–Li bonds (Figure 2).[32] The carbanion has a similar chiral C1-S conformation as *rac*-**18**·diglyme. The anionic C1 atom of *rac*-**20**·diglyme is somewhat pyramidalized as shown by the dihedral angles C2-C1-S-Ci of 86.5(6)° and Me-C1-S-Ci of –70.6(6)° and the sum of the bond angles at C1 of 356.0° (Table 1).

Table 1. Selected bond lengths [Å], bond angles [°] and dihedral angles [°] of the lithiated carbanions *rac*-**20**·diglyme and *rac*-**21**·PMDETA.

Parameter	*rac*-**20**·diglyme	*rac*-**21**·PMDETA
C1–S	1.639(7)	1.622(5)
C1–C2	1.440(9)	1.433(7)
C2–C3	1.35(1)	1.352(8)
S–O	1.455(5)	1.459(3)
	1.471(5)	1.478(3)
O–Li	1.91(1)	1.841(8)
	1.94(1)	
S–Ci(C)	1.790(6)	1.832(5)
S–$CH_3(CH_2)$	1.50(1)	1.509(8)
C1-C2-C3	128.0(7)	123.8(5)
S-C1-C2	120.9(5)	122.5(4)
C2-C1-C	117.5(7)	116.6(4)
S-C1-C	117.6(5)	120.7(4)
C1-S-Ci(*t*Bu)		114.7(2)
Ci(*t*Bu)-S-C1-C2	86.5(6)	–83.9(4)
Ci(*t*Bu)-S-C1-$CH_3(CH_2)$	–70.6(6)	90.0(5)
S-C1-C2-C3	–166.2(6)	–179.2(4)

The smaller dihedral angle Me-C1-S-Ci is perhaps caused to some extend by steric interaction between the methyl group at the C1 atom and the methyl group of the diglyme molecule.[18] The allyl unit of *rac*-**20**·diglyme shows with bond lengths C1–C2 of 1.440(9) Å and C2–C3 of 1.35(1) Å a similar bond length alternation as *rac*-**18**·diglyme (C1–C2 1.446(9) Å and C2–C3 1.352(9) Å). The C1–S bond of *rac*-**20**·diglyme is with 1.639(7) Å of similar length as the C1–S bonds of *rac*-**18**·diglyme (1.668(6) Å) and of the lithiated bicyclic allylic α-sulfony carbanions *rac*-**23**·diglyme (1.649(7) Å),[8] *rac*-**24**·diglyme (1.633(3) Å)[8] and *rac*-**25**·PMDETA (1.626(5) Å) (PMDETA = pentamethyldiethylene-triamine) (Figure 3),[9] which are also devoid of C–Li bonds. The C2–C3 unit of *rac*-**20**·diglyme is nearly in one plane with the C1–S unit as shown by the dihedral angle S-C1-C2-C3 of –166.2(6)°. Thus, the C=C double bonds of *rac*-**20**·diglyme and *rac*-**18**·diglyme are aligned in such a way as to allow for an interaction with the lone pair orbital at the anionic C1 atoms. The lithiated carbanion *rac*-**20**·diglyme adopts the *s-trans* conformation around the C1-C2 bond despite the presence of the methyl group at C1, which could in principle destabilize the *s-trans* conformation by steric interaction with the double bond.

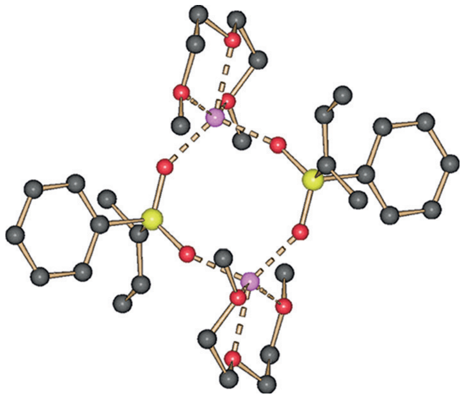


Figure 2. Structure of the lithiated acyclic allylic α-sulfonyl carbanion *rac*-**20**·diglyme in the crystal (colour code: black, carbon; red, oxygen; yellow, sulphur; pink, lithium).

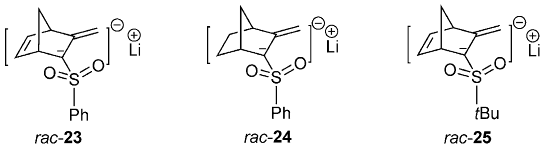


Figure 3. Lithiated bicyclic *s-cis* allylic α-sulfonyl carbanions.

Prior to our study, nothing was known about the structure of monocyclic lithiated allylic α-sulfonyl carbanions in the crystal. Therefore, the lithiated carbanions **21**·PMDETA and **22**·PMDETA were synthesized through deprotonation of the corresponding sulfones *rac*-**13** and *rac*-**15** with *n*BuLi in PMDETA and their structures determined by X-ray crystal structure analysis. PMDETA was chosen as ligand for the Li atom, because it favors the crystallization of monomeric lithiated α-sulfonyl carbanions by blocking three coordination sites at the

Li atom.[8,9] Single crystals of *rac*-**21**·PMDETA and *rac*-**22**·PMDETA were attained through recrystallization from THF. The crystalline lithiated carbanions are stable at room temperature under the exclusion of water and dioxygen. The lithiated six-membered cyclic allylic carbanion *rac*-**21**·PMDETA crystallized as a PMDETA-coordinated monomer.[32] Its Li atom is coordinated only to one O atom but not to a C atom of the allylic moiety (Figure 4).

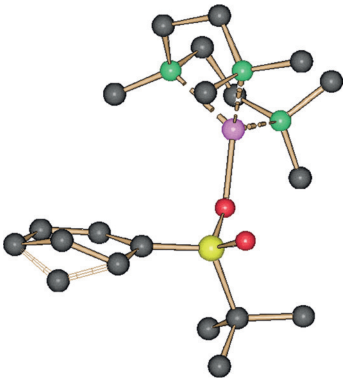


Figure 4. Structure of the monomeric lithiated six-membered cyclic allylic α-sulfonyl carbanion *rac*-**21**·PMDETA in the crystal (colour code: black, carbon; red, oxygen; yellow, sulphur; pink, lithium; green, nitrogen).

rac-**21**·PMDETA has the typical chiral C1–S conformation of *rac*-**18**·diglyme and *rac*-**20**·diglyme. Its anionic C1 atom is planar as revealed by dihedral angles CH_2-C1-S-*t*Bu of 90.0(5)° and C2-C1-S-*t*Bu of −83.9(4)° and the sum of the bond angles at C1 of 360.0°. In contrast, the anionic C atom of the saturated six-membered cyclic lithiated carbanion l{[$cC_6H_{10}SO_2Ph$]Li·digylme}$_2$ is significantly pyramidalized ($\Sigma\sphericalangle C1 = 353.0^\circ$).[18] The allylic unit of *rac*-**21**·PMDETA shows with C1–C2 1.433(7) Å and C2–C3 1.352(8) Å a similar bond length alternation as *rac*-**18**·diglyme and *rac*-**20**·diglyme. The C1–S bond of *rac*-**21**·PMDETA is with 1.622(5) Å of similar length as the C1–S bonds of *rac*-**18**·diglyme and *rac*-**20**·diglyme. The C2–C3 unit is in one plane with the C1–S unit as shown by the dihedral angle S-C1-C2-C3 of −179.2(4)°. Thus, the structural requirements for an optimal orbital interaction in the allylic unit are given. Atom C5 of *rac*-**21**·PMDETA is disordered, and atoms C4, C3, C1 and C6 almost lie in one plane as indicated by the dihedral angles C1-C2-C3-C4 of −4.4(8)° and C6-C1-C2-C3 of 6.7(8)°.

The crystal structure of the parent sulfone (*S*)-**13** (Figure 5)[32] was also determined in order to obtain information about the changes of the bonding parameter, which take place upon its conversion to *rac*-**21**·PMDETA. In the crystal two independent molecules of the sulfone exist, which mainly differ in regard to the C1–S conformation (conformers **A** and **B**). The cyclohexene rings of both molecules adopt half-chair conformations with the sulfonyl groups in pseudo-equatorial position.

A comparison of the bonding parameters of sulfone (*S*)-**13** and of *rac*-**21**·PMDETA shows that the C1–C2 bond of the lithiated carbanion is significantly shorter, while the C2–C3 bond is only slightly longer. On going from (*S*)-**13** to *rac*-**21**·PMDETA the bond angle C1-S-*t*Bu considerably widens. Generally, α-sulfonyl–carbanions have a larger bond angle C1-S-C than the corresponding sulfones.[8,9,18] The C1–C2 bonds of the bicyclic allylic carbanions *rac*-**23**·diglyme, *rac*-**24**·diglyme and *rac*-**25**·PMDETA are also significantly shorter and the C2–C3 bonds are only slightly longer than those of the corresponding sulfones.[8,9]

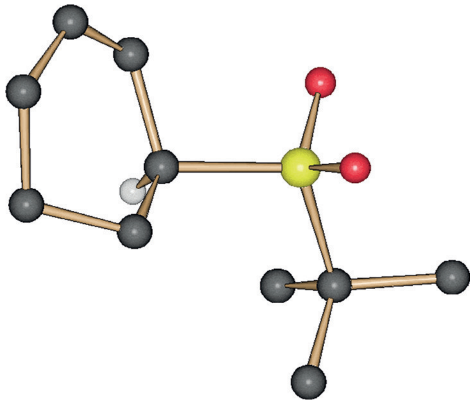


Figure 5. Structure and bonding parameters (in Å and°) of the cyclic sulfone (*S*)-**13** in the crystal. Conformer **A** (shown): S–*t*Bu 1.826(4), C1–S 1.826(2), C1–C2 1.515(5), C2–C3 1.327(3), C2-C1-C6 111.9(2), C2-C1-S 106.5(2), C6-C1-S 112.3(2), *t*Bu-S-C1-C2 −155.6(1), *t*Bu-S-C1-C6 81.6(2). Conformer **B** (not shown): S-*t*Bu 1.827(4), C1-S 1.811(2), C1-C2 1.505(3), C2-C3 1.325(3), C2-C1-C6 111.1(2), CH_2-C1-S 107.4(2), C2-C1-S 112.1(2), C1-S-*t*Bu 109.5(2), *t*Bu-S-C1-C2 −85.8(2), *t*Bu-S-C1-C6 151.8(1) (colour code: black, carbon; red, oxygen; yellow, sulphur; white, hydrogen).

From the crystal structure analyses follows that the monomeric and dimeric O,Li CIPs of lithiated allylic α-sulfonyl carbanions, which carry a C-substituent at C1, have nearly planar coordinated anionic C atoms. It seems interesting to note in this context that the O,Li CIPs of lithiated alkyl substituted benzylic α-sulfonyl carbanions have essentially planar anionic C atoms,[18,33–35] while the anionic C atoms of the O,Li CIPs of dialkyl substituted lithiated α-sulfonyl carbanions are strongly pyramidalized (half-way between sp^3 and sp^2 hybridization).[34,36]

The lithiated seven-membered cyclic allylic carbanion *rac*-**22**·PMDETA also crystallized as a PMDETA-coordinated monomer, the Li atom of which is coordinated to one O atom but not to the C1 atom of the allylic moiety (Figure 6).[32,37] It has a similar C1–S conformation as *rac*-**21**·PMDETA and an almost planar anionic C atom.

Structure in solution

The lithiated allylic α-*tert*-butylsulfonyl carbanions *rac*-**21**, *rac*-**22**, *rac*-**26**, *rac*-**27**, *rac*-**28**, *rac*-**29**, *rac*-**30** and *rac*-**31**, each containing two molecules of THF, were prepared upon reaction of the corresponding sulfones *rac*-**4**, *rac*-**5**, *rac*-**7**, *rac*-**12**, *rac*-**13**, *rac*-**14**, *rac*-**16** and *rac*-**17** with *n*BuLi in THF at low temperatures, removal of the solvent in vacuo at room temperature and dissolution of the oily or crystalline residues in [D_8]THF (Scheme 4).

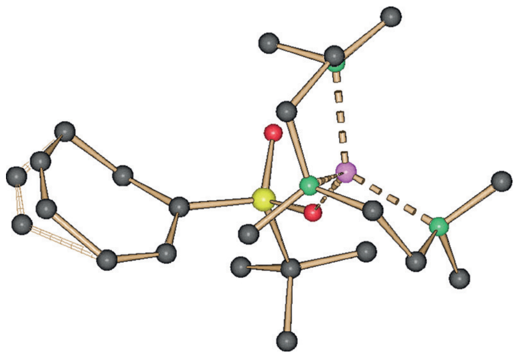
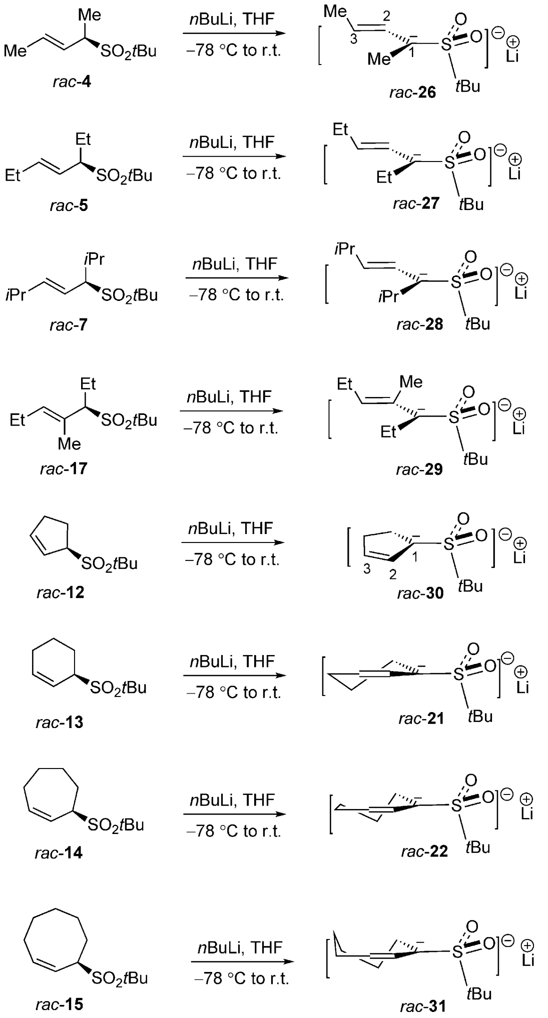


Figure 6. Structure of the monomeric lithiated seven-membered cyclic allylic α-sulfonyl carbanion *rac*-**22**·PMDETA in the crystal (colour code: black, carbon; red, oxygen; yellow, sulphur; pink, lithium; green, nitrogen).



Scheme 4. Synthesis of lithiated acyclic and cyclic allylic *S*-*tert*-butyl α-sulfonyl carbanions.

Similarly, ^{6}Li labeled *rac*-**27** was synthesized from *rac*-**5** and *n*Bu^{6}Li in [D$_8$]THF. The lithiated allylic carbanions were stable in solution at room temperature under the exclusion of water and dioxygen. The acyclic lithiated carbanions *rac*-**26**, *rac*-**27**, *rac*-**28** and *rac*-**29**, which are expected to form contact ion pairs (CIPs) in THF solution,[18,38] can adopt a large number of different structures including monomers and dimers. Most likely structures of the monomeric CIPs are **A**-**P** (Figure 7). The CIPs differ in respect to the configurations of the C1 and S atoms, the conformations around the C1–C2 and C1–S bonds, the position of the Li atom and the number and type of bonds between the Li atom and the carbanion and the number of coordinated THF molecules. The cyclic lithiated carbanions *rac*-**21**, *rac*-**22**, *rac*-**30** and *rac*-**31** can in principle attain structures of type **A**–**D** and **K**–**M** (with a *Z* configured CC double bond). The structures of *rac*-**21**·PMDETA and *rac*-**22**·PMDETA in the crystal can be regarded as monomeric CIPs of type **F** and **G**.

In addition to the monomeric CIPs the lithiated carbanions *rac*-**21**, *rac*-**22**, *rac*-**26**, *rac*-**27**, *rac*-**28**, *rac*-**29**, *rac*-**30** and *rac*-**31** can in principle form four different dimeric *s-trans* CIPs, having the (*anti*,*P*,*M*), (*anti*,*P(M)*,*P(M)*), (*syn*,*P*,*M*) and (*syn*,*P*(*M*),*P*(*M*)) configuration (not shown). The *rac*-**18**·diglyme and *rac*-**21**·diglyme crystallized as (*anti*,*P*,*M*)-configured dimers, whereby *P* and *M* designate the configurations of the carbanions and *anti*/*syn* specify the position of the substituents at the S atoms relative to the eight-membered ring composed of the S, O and Li atoms. In addition to the dimeric *s-trans* CIPs the corresponding dimeric *s-cis* and mixed *s-trans*/*s-cis* CIPs have to be considered as further possible species (not shown).

Monomer–dimer equilibrium

Cryoscopy of the ethyl substituted lithiated carbanion *rac*-**27**·2THF in THF at 164 K had yielded an aggregation number of $n=1.17\pm0.06$ ($c=50.0$ mmol kg^{-1}), which corresponds to an equilibrium composed of 83 ± 6% of monomeric CIPs and 17 ± 6% of dimeric CIPs.[30a,39] Cryoscopy of the unsubstituted lithiated allylic carbanion *rac*-**18** in THF at 164 K had given similar results ($n=1.11\pm0.06$).[12] The ratio of the monomer(s) and the dimer(s) of *rac*-**27** did not change in the concentration range from $c=0.10$ M to 0.50 M. A similar observation was made in the case of *rac*-**18**.[12]

Variable temperature ^{1}H NMR spectroscopy of *rac*-**27** in [D$_8$]THF showed at low temperatures a coalescence phenomenon, stemming from the hindered C1–S bond rotation (see below), and a second coalescence phenomenon at even lower temperatures. The ^{1}H NMR spectrum of *rac*-**27** in [D$_8$]THF displayed two species in a ratio of approximately 3:1 at −78 °C, which exhibited only small chemical shift differences for the signals of 2-H, 3-H and the methylene group at C1 of $\Delta\delta=0.01$ ppm. Similarly, ^{13}C NMR spectroscopy of *rac*-**27** in [D$_8$]THF showed a coalescence phenomenon at low temperatures. The ^{13}C NMR spectrum of *rac*-**27** featured two species in a ratio of approximately 3:1 at −78 °C, which also displayed only small chemical shift differences for Me, CMe$_3$, C1 and C3 of $\Delta\delta=0.07$–0.12 ppm. The two different species of *rac*-**27** are most likely the corresponding monomer(s) and the dimer(s), which are in rapid dynamic equilibrium even at low temperatures. In principle, the two equilibrium species of *rac*-**27** could also be the *s-trans* and *s-cis* isomers around the C1–C2 bond instead of the monomer(s) and dimer(s). However, the *s-trans* and *s-cis* isomers of carbanion *rac*-**27** are expected to exhibit much larger chemical shift differences for the allylic subunits than

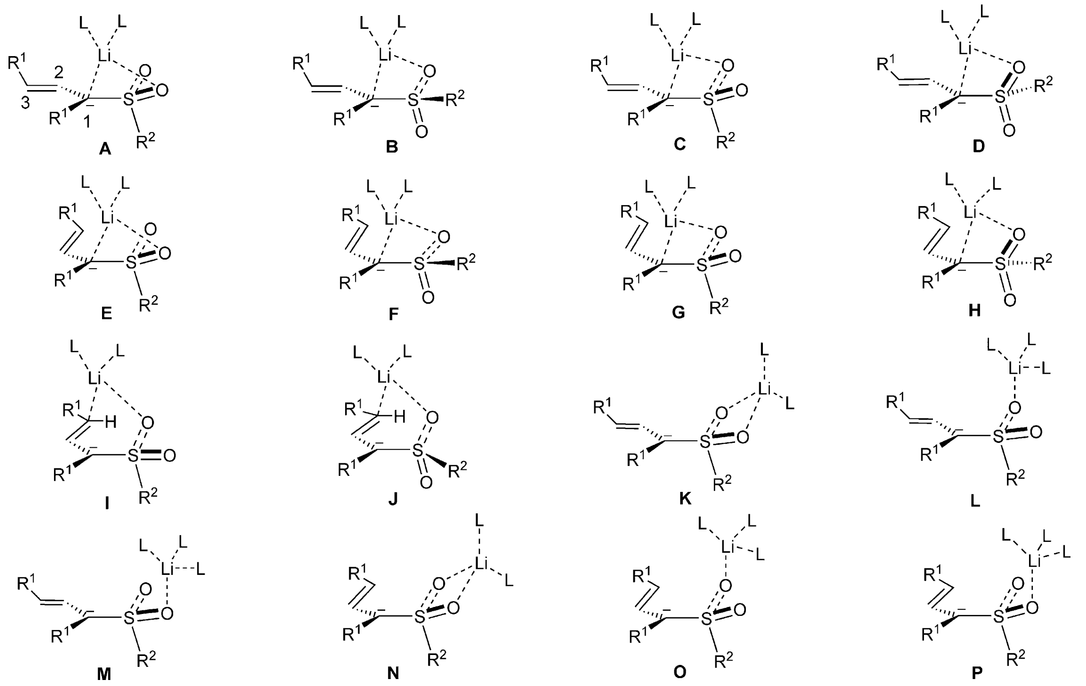
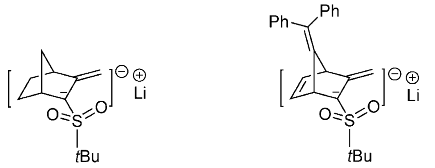


Figure 7. Possible structures of the monomeric CIPs of the lithiated acyclic allylic α-sulfonyl carbanions (L = THF).

those observed. For example, the *s-cis* and *s-trans* isomers of the CIPs as well as of the solvent separated ion pairs (SSIPs) of 1-(phenylthio)allyllithium and 1-(2-pyridylthio)allyllithium displayed chemical shift differences of $\Delta\delta$ (^{1}H) $\approx$ 0.20 ppm and $\Delta\delta$ (^{13}C) $\approx$ 10 ppm for the signals of the H and C atoms, respectively, of the allylic moieties.[40] Further support for the designation of the low-temperature species of *rac*-**27** as monomer(s) and dimer(s) comes from previous ^{1}H and ^{13}C NMR studies of the lithiated bicyclic allylic α-sulfonyl carbanions *rac*-**25**, *rac*-**32** and *rac*-**33** (cf. Figure 3, Figure 8) in [D$_8$]THF, which cannot engage in a *s-trans*/*s-cis* equilibrium.[8,9] The NMR spectra of the lithiated bicyclic carbanions displayed at −78 °C monomers and dimers, having similar small chemical shift differences as *rac*-**27**, in ratios comparable to those found by cryoscopy. In addition, ^{1}H and ^{13}C NMR investigations of lithiated alkyl substituted benzylic α-sulfonyl carbanions in [D$_8$]THF at −78 °C also showed the existence of two species, most likely monomers and dimers, having only small chemical shift differences, in ratios comparable to those determined by cryoscopy for the monomers and dimers.[18] Variable temperature ^{1}H and ^{13}C NMR spectroscopy of the diisopropyl substituted carbanion *rac*-**28** and the diethyl-methyl substituted carbanion *rac*-**29** in [D$_8$]THF showed in addition to coalescence phenomena, originating from the hindered C1–S bond rotation (see below), further coalescence phenomena and in each case two species at −85 °C, most likely monomers and dimers, which exhibited only small chemical shift differences.



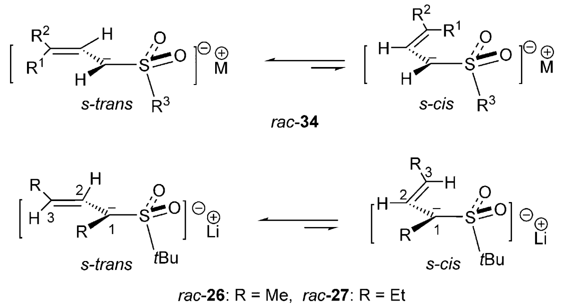
rac-**32** *rac*-**33**

Figure 8. Lithiated bicyclic *s-cis* allylic *S-tert*-butyl α-sulfonyl carbanions.

C1–C2 conformation

The lithiated allylic α-sulfonyl carbanion *rac*-**18·**diglyme, which carries a H atom at C1, has in the crystal the *s-trans* conformation around the C1–C2 bond. It also preferentially adopts in THF solution at room temperature the *s-trans* conformation as indicated by the magnitude of the coupling constant ^3J(1-H,2-H) of 10.9 Hz. Generally, the CIPs and SSIPs of metalated allylic α-sulfonyl carbanions of type *rac*-**34** (Scheme 5), carrying a H atom at the anionic C1 atom, prefer the *s-trans* conformation around the C1–C2 bond as shown by the magnitudes of ^3J(1-H,2-H), which are in the range of 10.5 to 11.0 Hz (Supporting Information, Table S1).[5,10,11] ^{1}H,^{1}H NOE experiments of the dimethyl substituted allylic α-sulfonyl carbanion *rac*-**34** (M = Li, R^1 = R^2 = Me; R^3 = Ph) in [D$_8$]THF at room temperature had also given evidence for a preferred *s-trans* conformation around the C1–C2 bond.[10c] Although the magnitudes of ^3J(1-H,2-H) for the *s-cis* conformers of *rac*-**34** are not known, it is expected that they are much smaller than those of the *s-trans* conformers. For example, coupling constants ^3J(1-H,2-H) of 11.1 Hz and 4.8 Hz had been measured for the *s-trans* and *s-cis* conformers, respectively, of the CIPs and SSIPs of 1-(phenylthio)allyllithium.[40] Typically, lithiated allylic α-sulfenyl carbanions from in THF equilibrium mixtures of *s-cis* isomers as the major and *s-trans* isomers as the minor species.[12,40–42]

The lithiated allylic *S*-phenyl carbanion *rac*-**20·**diglyme, which carries a methyl group at the anionic C atom, has in the



Scheme 5. Equilibrium of *s-trans* and *s-cis* Isomers of lithiated allylic α-sulfonyl carbanions.

crystal also the *s-trans* conformation around the C1–C2 bond. $^1H,^1H$ NOE experiments of the C1 methyl substituted *S-tert*-butyl carbanion *rac*-**26** in [D_8]THF at room temperature showed strong effects between the methyl group at the anionic C1 atom and 3-H, only a weak effect between the methyl group at C1 and 2-H and a medium effect between 2-H and the *tert*-butyl group (Scheme 5). These results would be compatible with a dynamic conformational equilibrium of *rac*-**26**, in which the *s-trans* isomer is the major and the *s-cis* isomer is the minor species. Similar $^1H,^1H$ NOE experiments of the C1 ethyl substituted *S-tert*-butyl carbanion *rac*-**27** in [D_8]THF at room temperature gave strong effects between the H atoms of the ethyl group at C1 and 3-H, medium effects between 2-H and the *tert*-butyl group, medium effects between the ethyl group at C1 and the *tert*-butyl group but no effect between the C1 ethyl group and 2-H. These results indicate that *rac*-**27** almost exclusively adopts the *s-trans* conformation.

Site of the Li atom in the CIP

While monomeric CIPs of type **K**–**P** have like the corresponding dimers only O–Li bonds, monomeric CIPs of type **A**–**J** exhibit O–Li and C–Li bonds. In order to obtain structural information about the CIPs of *rac*-**27**, $^6Li,^1H$ HOESY experiments were carried out in [D_8]THF at room temperature and at −90 °C. Because of the similar chemical shifts of the monomers and dimers, a distinction between both in the 2D $^6Li,^1H$ HOESY experiment was not possible and thus only averaged information was obtained. The ^6Li NMR spectrum showed a single peak at room temperature and at −90 °C. The 2D $^6Li,^1H$ HOESY spectra of ^6Li labeled *rac*-**27** at room temperature and at −90 °C revealed correlations of the Li atom with the *tert*-butyl group, the 2-H atom and the methylene group at C1. A correlation between the Li atom and 3-H was not observed. These correlations would be compatible with fast dynamic equilibria between O,C,Li CIPs of type **A**–**D** and O,Li CIPs of type **K**–**M**. $^6Li,^1H$ NOE experiments of *rac*-**34** ($M = Li$, $R^1 = R^2 = Me$; $R^3 = Ph$) in [D_8]THF at room temperature had also pointed to equilibria between O,Li CIPs and O,C,Li CIPs.[10c] Previous $^6Li,^1H$ NOE studies of lithiated benzylic α-trifluoromethylsulfonyl carbanions in [D_8]THF at low temperatures had indicated the existence of equilibria between O,Li CIPs as major and O,C,Li CIPs as minor components.[20] While the ^{13}C NMR spectrum of *rac*-**27** at −90 °C showed besides the monomers and dimers no further species, the spectra of the bicyclic *s-cis* allylic α-sulfonyl carbanions *rac*-**25**, *rac*-**32** and *rac*-**33** in [D_8]THF had revealed at −90 °C besides the monomers and dimers further rapidly equilibrating species, most likely different CIPs.[8,9] Similar observations were made by ^{13}C NMR spectroscopy of lithiated benzylic α-*tert*-butylsulfonyl carbanions in [D_8]THF at −90 °C.[18]

Mixed aggregate with lithium ethenolate

The use of an excess of nBu^6Li in the deprotonation of *rac*-**5** in [D_8]THF led, besides *rac*-**27**, to the formation of deuterated lithium ethenolate (≈90% D)[43] as shown by ^2H and ^1H NMR spectroscopy. Interestingly, the lithiated carbanion *rac*-**27** formed besides the monomer(s) and dimer(s) a mixed aggregate with lithium ethenolate in [D_8]THF, according to ^1H, ^{13}C and ^6Li NMR spectroscopy and 2D $^1H,^6Li$ HOESY experiments at −78 °C.[30a,44,45] 2D ^6Li EXSY experiments of the mixture of monomer(s), dimer(s) and mixed aggregate at −90 °C revealed an exchange of the Li atoms of the three species.[30a]

Allylic stabilization of the negative charge

The acidities of allyl phenylsulfone ($\Delta pK_a = 6.5$) and benzyl phenylsulfone ($\Delta pK_a = 5.6$) are higher than the acidity of methyl phenylsulfone (K^+, DMSO).[46] This is commonly attributed to an increased stabilization of the corresponding allylic and benzylic α-sulfonyl carbanions by conjugation of the negative charge with the double bond and phenyl group, respectively. X-Ray crystal structure analyses of *rac*-**20**·diglyme and *rac*-**21**·PMDETA had revealed dihedral angles S-C1-C2-C3 of 166.2 (6)° and −179.2 (4)°. Thus, the orbitals of the allylic units are properly aligned for an additional stabilization of the carbanions by conjugative interaction. Table 2 lists the ^1H and ^{13}C chemical shifts of the allylic moieties of *rac*-**21**, *rac*-**22**, *rac*-**26**, *rac*-**27**, *rac*-**28**, *rac*-**29**, *rac*-**30** and *rac*-**31** and the shift variations ($\Delta\delta$), which were observed in [D_8]THF on going from the sulfones *rac*-**4**, *rac*-**5**, *rac*-**7**, *rac*-**12**, *rac*-**13**, *rac*-**14**, *rac*-**16** and *rac*-**17** to the corresponding lithiated carbanions. An inspection of Table 2 reveals the following qualitative shift variations: 1) small variations in the C1 and C2 signals, 2) strong up-field shifts of the C3 signals, 3) medium down-field shifts of the 2-H signals and 4) strong up-field shifts of the 3-H signals. Similar chemical shift variations had been recorded for the bicyclic carbanions *rac*-**23**, *rac*-**24**, *rac*-**25**, *rac*-**32** and *rac*-**33**[8] and for allylic α-sulfonyl carbanions carrying a H atom at the anionic C1 atom (Supporting Information, Table S1).[10–12] Lithiated allylic α-sulfonimidoyl carbanions *rac*-**35**,[3,10c,21b,47] lithiated allylic sulfenyl carbanions[12,40–42] and lithiated allylic diaminophosphonyl carbanions[48] show similar NMR spectroscopic features.

The shifts variations recorded for the allylic α-sulfonyl carbanions indicate 1) a hybridization of the anionic C atoms somewhere between sp^3 and sp^2, 2) the accumulation of negative charge at C3, 3) the accumulation of positive charge at C2 and 4) the negative charge at C1. Charge distributions of the type $C1^-$-$C2^+$-$C3^-$, which are the result of allylic conjugation and/or polarization of the double bond by the accumulation of

Table 2. Selected ^{1}H and ^{13}C NMR data (δ in ppm) of the lithiated allylic *S-tert*-butyl α-sulfonyl carbanions *rac*-**21**, *rac*-**22**, *rac*-**26**, *rac*-**27**, *rac*-**28**, *rac*-**29**, *rac*-**30** and *rac*-**31** in $[D_8]$THF at room temperature.[a]

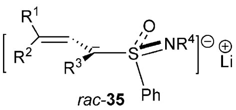
Lithiated carbanion	– *C-1($\Delta\delta$)*	2-H($\Delta\delta$) *C-2($\Delta\delta$)*	3-H($\Delta\delta$) *C-3($\Delta\delta$)*
rac-**26**	– *52.7(−4.1)*	6.25(0.69) *134.8(5.7)*	3.73(−2.03) *90.7(−37.5)*
rac-**27**	– *61.3(−4.0)*	6.14(0.69) *129.0(4.5)*	4.01(−1.74) *100.1(−39.4)*
rac-**28**	– *60.7(−4.9)*	6.03(0.53) *129.0(8.7)*	4.81(−0.69) *107.5(−36.9)*
rac-**29**	– *63.3(−7.2)*	– *134.6(4.2)*	4.33(−1.21) *107.1(−29.6)*
rac-**30**	– 62.4(−2.4)	6.14(0.07) *137.6(13.8)*	4.34(−1.47) *101.6(−37.5)*
rac-**21**	– 55.5(0)	6.14(0.15) *131.3(−2.5)*	4.19(−1.51) *95.7(−26.2)*
rac-**22**	– 62.5(3.0)	6.25(0.25) *134.0(−1.5)*	4.20(−1.80) *99.8(−29.3)*
rac-**31**	– 62.0(6.0)	6.30(0.42) *136.6(3.4)*	3.97(−1.71) *95.5(−32.1)*

[a] $\Delta\delta = \delta_{\mathrm{carbanion}} - \delta_{\mathrm{sulfone}}$.

negative charge at C1, lead to coulombic stabilization. Calculations of *rac*-**23** and *rac*-**24** had yielded a similar charge distribution in the allylic moieties with an unequal distribution of the negative charge between C1 and C3.[8,9] However, despite the conjugative interaction in *rac*-**18**·diglyme, *rac*-**20**·diglyme, *rac*-**21**·PMDETA, *rac*-**23**·diglyme, *rac*-**24**·diglyme and **25**·PMDETA, their allylic units show strong bond length alternation with long C1–C2 and short C2–C3 bonds.

Interestingly, the up-field shift of the signal of 3-H of the isopropyl substituted allylic carbanion *rac*-**28** is significantly smaller than the up-field shifts of 3-H of the other allylic α-sulfonyl carbanions.

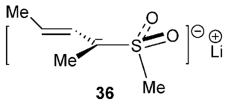
In summary, the NMR spectroscopic investigations of the lithiated allylic *S-tert*-butyl carbanions *rac*-**26**, *rac*-**27**, *rac*-**28** and *rac*-**29** in THF point to the existence of rapid equilibria not only between monomers and dimers, but also between monomeric O,Li and O,C,Li CIPs having the *s-trans* (major) and *s-cis* (minor) conformation. Thus with the exception of the monomers and dimers only averaged NMR data were obtained. This holds also true for the other lithiated allylic α-sulfonyl carbanions described in this work.


rac-**35**

Previous investigations of lithiated allylic α-sulfonimidoyl carbanions *rac*-**35**, the aza analogs of the sulfonyl carbanions, in the crystalline phase and in THF solution had also shown a preference for the *s-trans* conformation, equilibria between O(N),Li and O(N),C,Li CIPs, and a similar C1–S conformation.[10c,21b,47,49,50]

Theoretical structures of a lithiated allylic α-sulfonyl carbanion

In order to corroborate the structural information gathered of the CIPs of *rac*-**26** and *rac*-**27** in $[D_8]$THF solution by NMR spectroscopy, ab initio calculations of the lithiated trimethyl substituted allylic α-sulfonyl carbanion **36** were carried out as model compound. In particular, information was sought about the viability and energies of monomeric CIPs of the type shown in Figure 6.


36

The relative energies of all isomers of **36** obtained at different levels of accuracy are listed in Table 3. Selected calculated structural parameters of interest, dipole moments and energies are given in Tables 4–6. The corresponding total energies of the isomers are listed in Table S2 of the supporting information, were also the optimized Cartesian coordinates of all local minima are listed.

Table 3. Relative energies of the isomers **A**, **B**, **E**, **J**, **K** and **N** of the lithiated allylic α-sulfonyl carbanion **36** at different levels of theory in kcal mol^{-1}. ε_0 is the zero point energy.

Isomer	MP2/6-31+G*//MP2/6-31+G*	MP2/6-31+G*//MP2/6-31+G*+ε_0	MP2/6-31+G*//MP2/6-31+G*+SCRF[a]	MP2/6-31+G*//MP2/6-31+G*+SCRF[a]+ε_0
s-trans/O,C1,Li (**36A**)	±0.0	±0.0	±0.0	±0.0
s-trans/O,Li (**36K**)	3.23	2.74	2.82	2.33
s-trans/O,C1,Li (**36B**)	6.59	6.47	2.87	2.75
s-cis/O,C3,Li (**36J**)	6.23	6.06	4.03	3.86
s-cis/O,C1,Li (**36E**)	3.64	3.45	4.31	4.12
s-cis/O,Li (**36N**)	6.59	5.92	6.41	5.74

[a] $\varepsilon = 7.4257$, THF, PCM model.[51]

At all levels of theory the *s-trans*/O,C1,Li isomer **36A** is the most stable species closely followed by the *s-trans*/O,Li isomer **36K** (Figure 9), which is 2.82 and 2.33 kcal mol^{-1} higher in energy at the MP2/6-31+G*//MP2/6-31+G*+SCRF and MP2/6-31+G*//MP2/6-31+G*+SCRF+ε_0 level, respectively (Table 3). Applying the same methods, the *s-trans*/O,C1,Li isomer **36B** is the next one on the energy scale (2.87 and 2.75 kcal mol^{-1}). The *s-trans*/O,C1,Li isomer **36A** and the *s-trans*/O,C1,Li isomer **36B** differ in regard to the C1–S conformation. A strong solvent effect is observed for **36B** which is the least stable one of all isomers without the SCRF corrections (ΔE_{SCRF})[51] but is energetically similar to the *s-trans*/O,Li isomer **36K** when SCRF corrections are included (2.87 and 2.75 kcal mol^{-1}). The significant bulk effect of the solvent in this case is due to the much higher dipole moment of the *s-trans*/O,C1,Li isomer **36B** ($\mu = 9.296$ D) compared with the *s-trans*/O,Li

Table 4. Selected O(C)–Li bond lengths [Å] and the sums of bond angles Σ [°] at the formally anionic carbon atom C1 in the geometries optimized at the MP2/6-31+G* level of the isomers **A**, **B**, **E**, **J**, **K** and **N** of the lithiated allylic α-sulfonyl carbanion **36**. Interatomic distances that might be considered bonds are in italics. $\Sigma_{n^*}\Delta E_{nn^*}^{(2)}$ is the energy of interaction between the anionic lone pair (n) and the formally empty atomic orbitals (n^*) at the Li atom, and $\Delta E_{n\pi^*}^{(2)}$ is the corresponding energy of interaction between the anionic lone pair and the π* orbital of the CC double bond (in kcal mol^{-1}).

Isomer	r(O–Li)	r(C1–Li)	r(C3–Li)	Σ∢C1	$\Sigma_{n^*}\Delta E_{nn^*}^{(2)[a]}$	$\Delta E_{n\pi^*}^{(2)}$
s-trans/O,C1,Li (**36 A**)	*1.979/ 3.212*	*2.284*	4.453	346.69	−28.04	−40.22
s-trans/O,Li (**36 K**)	*2.069/ 2.015*	3.407	5.495	356.41	−1.94	−57.95
s-trans/O,C1,Li (**36 B**)	*1.944/ 3.937*	*2.210*	3.636	342.52	−11.79	−41.66
s-cis/O,C3,Li (**36 J**)	*1.949/ 3.930*	*2.341*	*2.438*	349.79	−24.58	−59.17
s-cis/O,C1,Li (**36 E**)	*1.995/ 3.184*	*2.282*	4.374	344.60	−29.60	−37.47
s-cis/O,Li (**36 N**)	*2.044/ 2.024*	3.441	4.730	353.36	−2.49	−53.13

[a] $\Delta E_{nn^*} = -q_n \cdot \langle n|\boldsymbol{F}|n^*\rangle^2/(\varepsilon_{n^*}-\varepsilon_n)$, where ***F*** is the Fock operator of the molecule and q_n the occupation number of the lone pair. ε_{n^*} and ε_n are the NBO orbital energies of the n^* orbitals at Li and the anionic lone pair (n) at C1, respectively.

Table 5. Selected calculated (MP2/6-31+G*) bond lengths (Å) and dihydral angles (°) of the isomers **A**, **B**, **E**, **J**, **K** and **N** of the lithiated allylic α-sulfonyl carbanion **36**.

Isomer	C1–S	C1–C2	C2–C3	S-C1-C2-C3	Me-S-C1-C2	Me-C1-S-O
s-trans/O,C1,Li (**36 A**)	1.699	1.457	1.357	154.5	−85.0	−58.1
s-trans/O,Li (**36 K**)	1.655	1.445	1.360	165.6	−82.5	−41.5
s-trans/O,C1,Li (**36 B**)	1.722	1.463	1.359	−155.1	−177.1	159.0
s-cis/O,C3,Li (**36 J**)	1.710	1.448	1.370	11.8	−170.1	−72.5
s-cis/O,C1,Li (**36 E**)	1.700	1.469	1.357	−20.9	−78.5	−56.1
s-cis/O,Li (**36 N**)	1.656	1.456	1.361	−25.3	−68.7	−36.5

Table 6. Calculated (MP2/6-31+G*) dipole moments (μ) of the isomers **A**, **B**, **E**, **J**, **K** and **N** of the lithiated allylic α-sulfonyl carbanion **36** (in D).

Isomer	μ
s-trans/O,C1,Li (**36 A**)	5.605
s-trans/O,Li (**36 K**)	6.316
s-trans/O,C1,Li (**36 B**)	9.296
s-cis/O,C3,Li (**36 J**)	8.924
s-cis/O,C1,Li (**36 E**)	5.653
s-cis/O,Li (**36 N**)	6.038

isomer **36 K** ($\mu = 6.316$ D), which is the second stable species without the SCRF corrections. The stabilization energies due to the bulk solvent effects are $\Delta E_{\mathrm{SCRF}} = -12.20$ for the *s-trans*/O,C1,Li isomer **36 B** and $\Delta E_{\mathrm{SCRF}} = -8.89$ kcal mol^{-1} for the *s-trans*/O,Li isomer **36 K**, respectively. A similarly strong, although due to a slightly lower dipole moment weaker, effect of the SCRF corrections is obtained for the *s-cis*/O,C3,Li isomer **36 J** ($\mu = 8.924$ D, $\Delta E_{\mathrm{SCRF}} = -10.68$ kcal mol^{-1}) (Figure 10). Of the *s-cis* isomers *s-cis*/O,Li (**36 N**), *s-cis*/O,C1,Li (**36 E**) and *s-cis*/O,C3,Li (**36 J**) the later one, which has a C–Li bond involving the terminal C3 atom, has the lowest energy when the solvent is included. A DFT calculation of *s-cis* isomers of the lithiated allylic α-sulfonyl carbanion *rac*-**18**·2 THF had found a structure similar to **36 J** to be the most stable one.[12]

Ab initio calculation of the lithiated benzylic α-*tert*-butylsulfonyl carbanion $[\mathrm{PhC(Me)SO_2}t\mathrm{Bu}]\mathrm{Li}\cdot(\mathrm{Me_2O})_2$,[20] the Li atom of which carries two ether molecules, had also yielded an energetic preference for a CIP structure with O–Li and C1–Li bonds of type **A**. However, a similar calculation of the analogous lithiated α-trifluormethylsulfonyl carbanion $[\mathrm{PhC(Me)SO_2CF_3}]\text{-}\mathrm{Li}\cdot(\mathrm{OMe_2})_2$[20] showed a CIP structure of type **K** with two O–Li

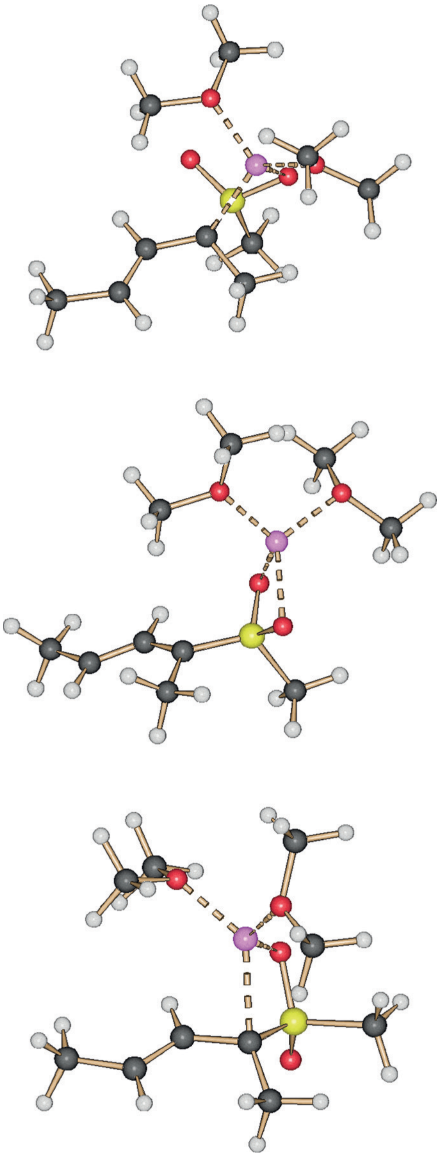


Figure 9. View of the calculated structures (MP2/G-31+G*) of the *s-trans* isomers **A**, **K** and **B** of the lithiated allylic α-sulfonyl carbanion **36** (colour code: black, carbon; red, oxygen; yellow, sulphur; pink, lithium; white, hydrogen). Top, **36 A**; middle, **36 K**; bottom, **36 B**.

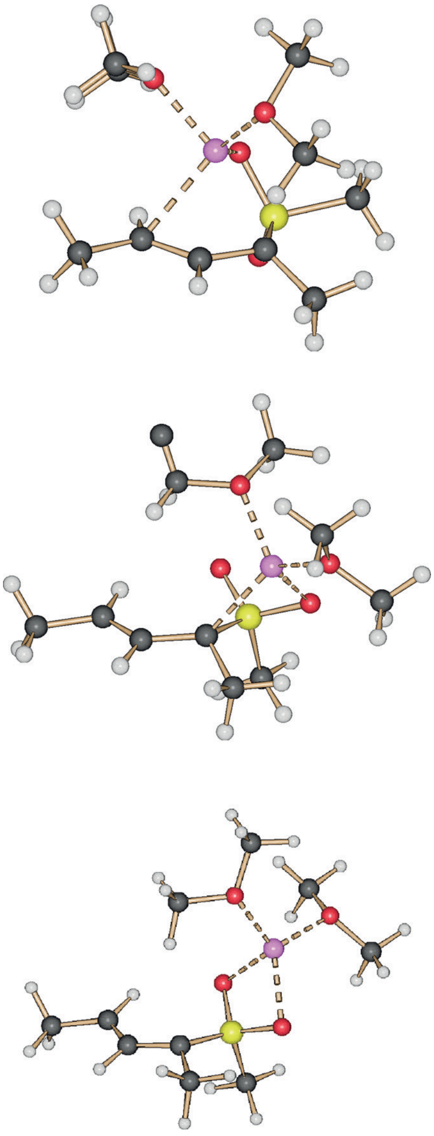


Figure 10. View of the calculated structures (MP2/G-31+G*) of the *s-cis* isomers **J**, **E** and **N** of the lithiated allylic α-sulfonyl carbanion **36** (colour code: black, carbon; red, oxygen; yellow, sulphur; pink, lithium; white, hydrogen). Top, **36 J**; middle, **36 E**; bottom, **36 N**.

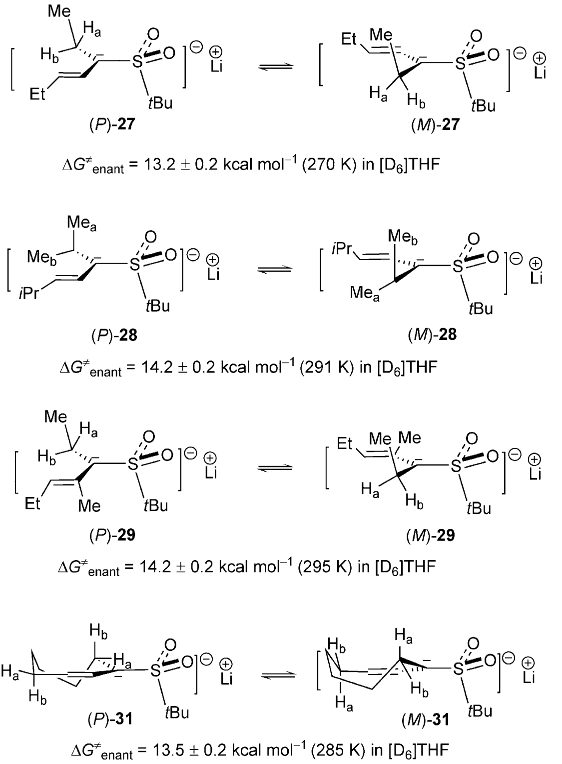
bonds to be the most stable one. While an initio calculation of $[PhC(H)SO_2Ph]Li{\cdot}(OMe_2)_2$ also gave a structure of type **A**, that of $[PhC(H)SO_2Ph]Li{\cdot}(OMe_2)_3$, which carries three ether molecules at the Li atom, gave a structure of type **L** having no C–Li bond.[52] A DFT calculation of $[MeC(H)SO_2Ph]Li{\cdot}(OMe_2)_2$ found a structure of type **A** to be more stable than a structure of type **K**.[35]

The calculated (MP2/6-31+G*) values of the interatomic distances between the anionic carbon atoms (C1) and the Li atoms in Table 4 show that except for *s-trans*/O,Li (**36 K**) and *s-cis*/O,Li (**36 N**) there are most likely bonding interactions between these atoms in the remaining structures, and the same is true for at least one of the Li–O distances. The strongest pyramidalization of the formally anionic carbon atom C1, which correlates with the shortest calculated C1–Li distance (2.210 Å), was obtained for the *s-trans*/O,C1,Li isomer **36 B**. At 342.52° the sum of bond angles at C1 is closest to the value for a sp^3-hybridized carbon atom (328.41°). In the *s-trans*/O,Li structure the sum of bond angles at the corresponding carbon atom amounts to 356.41° and is, therefore, close to the value for an atom in a perfectly planar environment. We thought that the degree of pyramidalization might correlate with the results of NBO analyses[53] of the corresponding molecular wave functions especially with the second-order energies of interaction between the anionic lone pair (*n*) with the formally empty orbitals at the Li atom (*n**), $\Sigma_{n^*}\Delta E_{nn^*}^{(2)}$, and between the lone pair and the π* anti-bond of the olefinic double bond (π*), $\Delta E_{n\pi^*}^{(2)}$. The corresponding values are listed in columns six and seven of Table 4. However, it is obvious that there is no such throughout correlation between the degree of pyramidalization and these energetic quantities. Irrespective of the presence or absence of a C–Li bond the interaction of the lone pair with the π* orbital of the C=C double bond is in all CIPs energetically much more favorable than that with the “empty” orbitals at the Li atom. The allylic units of the isomers of **36** show a strong bond length alternation (Table 5) and all isomers adopt a C1–C2 conformation, which allows for an interaction of the lone-pair at C1 with the double bond. The C1–S bond lengths of the isomers show marked differences. The isomers with only O–Li bonds have the shortest C1–S bonds (**36 K**, **36 N**), while the isomers in which the lone-pair orbital at C1 is approximately periplanar to a S–O bond (**36 B**, **36 J**) have the longest C1–S bonds. Isomers **36 A**, **36 K**, **36 E** and **36 N** adopt a C1–S conformation in which lone-pair orbital at C1 is approximately periplanar to the S-Me bond, while in isomers **36 B** and **36 J** the lone-pair orbital is approximately periplanar to a S–O bond.

In summary, the by far most stable isomer of the *S*-methyl substituted lithiated carbanion **36** is the O,C,Li CIP **A**, having besides the *s-trans* conformation C1–Li and O–Li bonds, including the effect of the solvent. The next stable isomer is the O,Li CIP **K**, which has also the *s-trans* conformation and only O-Li bonds followed by the O,C,Li CIP **B**, which is similar in energy and has also the *s-trans* conformation and O,Li as well as C1–Li bonds. All *s-cis* isomers of **36** are very much higher in energy. Based on the relative energies of the CIP structures of **36** and the ^{6}Li,^{1}H HOESY experiments of *rac*-**27**, it is much likely that the *S-tert*-butyl derivatives *rac*-**26**, *rac*-**27**, *rac*-**28** and *rac*-**29** also preferentially form in THF solution rapidly equilibrating *s-trans* CIPs (vide infra) of type **A** and **K** together with perhaps CIPs of type **L** and **M**.

Configurational stability

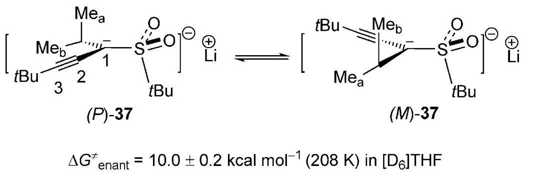
The configurational stability of lithiated alkyl-phenyl and dialkyl substituted α-sulfonyl carbanions is determined by the height of the barrier towards rotation around the C1–S bond, which is mainly an enthalpic process.[14,18,20] We had previously obtained estimates of the height of the enantiomerization barrier through ^{1}H DNMR spectroscopy of derivatives containing diastereotopic H atoms that undergo topomerisation during C_α–S bond rotation.[14,15,18–20] ^{1}H DNMR spectroscopy of the ethyl-substituted lithiated carbanion *rac*-**27**, which carries the diastereotopic H_a and H_b atoms that undergo topomerisation during enantiomerization, in [D_8]THF under selective decoupling of the methyl groups gave an estimated enantiomerization barrier[54] $\Delta G^{\neq}_{\text{enant}} = 13.2 \pm 0.2$ kcal mol^{-1} at the coalescence temperature of 270 K (Scheme 6). The introduction of an isopropyl group at the anionic C1 atom instead of the ethyl group increased the barrier. ^{1}H DNMR spectroscopy of the isopropyl-substituted carbanion *rac*-**28** in [D_8]THF under selective decoupling of the H atom of the isopropyl group gave an estimated enantiomerization barrier $\Delta G^{\neq}_{\text{enant}} = 14.2 \pm 0.2$ kcal mol^{-1} at the coalescence temperature of 291 K. ^{1}H DNMR spectroscopy of carbanion *rac*-**29**, which carries an ethyl group at C1 and a methyl group at C2, in [D_8]THF under selective decoupling of the methyl groups gave an estimated enantiomerization barrier $\Delta G^{\neq}_{\text{enant}} = 14.2 \pm 0.2$ kcal mol^{-1} at the coalescence temperature of 295 K.



Scheme 6. Thermodymanic parameters of the enantiomerization of lithiated allylic α-sulfonyl carbanions.

Interestingly, ^{1}H DNMR spectroscopy of the lithiated propargylic α-sulfonyl carbanion *rac*-**37** (Scheme 7) in [D_8]THF had previously given a significantly lower enantiomerization barrier of only $\Delta G^{\neq}_{\text{enant}} = 10.0 \pm 0.3$ kcal mol^{-1} (208 K).[39,55]

The ^{1}H NMR spectra of the six-membered cyclic allylic carbanion *rac*-**21** in [D_8]THF showed no line-broadening in the temperature range from room temperature to −80 °C. Similarly, the ^{13}C NMR spectrum of *rac*-**21** in [D_8]THF remained unchanged in this temperature range. In contrast, the ^{1}H NMR spectra of the eight-membered cyclic allylic carbanion *rac*-**31** in [D_8]THF displayed coalescence phenomena for the signals of 4-H and 8-H. The estimation of the barrier gave $\Delta G^{\neq}_{\text{enant}} = 13.5 \pm 0.2$ kcal mol^{-1} at the coalescence temperature of 285 K. The enantiomerization of *rac*-**31** needs in addition to the C_α–S bond rotation a ring inversion, the barrier of which should be, however, much lower than the barrier estimated for C_α–S bond rotation.[56]



Scheme 7. Thermodymanic parameter of the enantiomerization of the lithiated propargylic α-sulfonyl carbanion **37**.

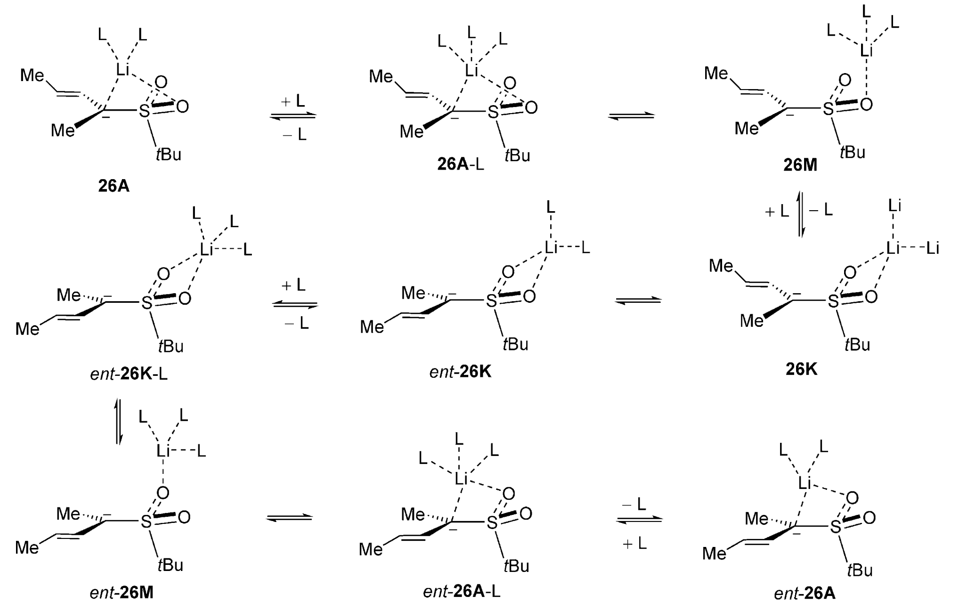
While the enantiomerization of the O,Li CIPs **K** of **26**-**29** and **36** involves two steps, rotation around the C1–S bond and C1 inversion, that of the O,C,Li CIPs **A** has to entail, in addition to C1–S bond rotation and C1 inversion, the cleavage and the reformation of the C1–Li and O–Li bonds (Scheme 8). A fast solvent assisted topomerisation of the Li atom can be envisioned for the cleavage and reformation of the bonds. Thus, coordination of a THF molecule to the O,C,Li CIP **26 A** gives **26 A**–**L**, which experiences a de-coordination of the Li atom from C1 to form **26 M**, because of the weaken C1–Li bond. Through loss of a THF molecule **26 M** is converted to the O,Li CIP **26 K** which undergoes C1–S bond rotation to furnish *ent*-**26 K**. The coordination of a THF molecule to the later yields *ent*-**26 K**–**L** and weakens the C1-Li bond, which leads to a de-coordination of the Li atom from the O atom to yield *ent*-**26 M**. Ring closure of *ent*-**26 M** with formation of the C1-Li bond gives *ent*-**26 A**–**L**, which upon loss of a THF molecule is converted to *ent*-**26 A**. The barriers for the de-coordination of the Li atom from C1 and its coordination to the O atom should be lower in energy than the barrier for C1–S bond rotation since previous studies of the CIPs and SSIPs of lithiated benzylic α-sulfonyl carbanions had found similar enantiomerization barriers for both species.[14,18,20] In accordance with the proposed fast C,O migration of the Li atom of the lithiated allylic α-sulfonyl carbanions in [D_8]THF is the failure to observe by NMR spectroscopy, even at low temperatures, different CIPs and ^{13}C,^{6}Li couplings.

The enantiomerization of CIPs **K** and **A** of the cyclic lithiated allylic α-sulfonyl carbanions **21**, **22**, **30** and **31** should proceed in a similar manner except that as an additional step a ring inversion is required.

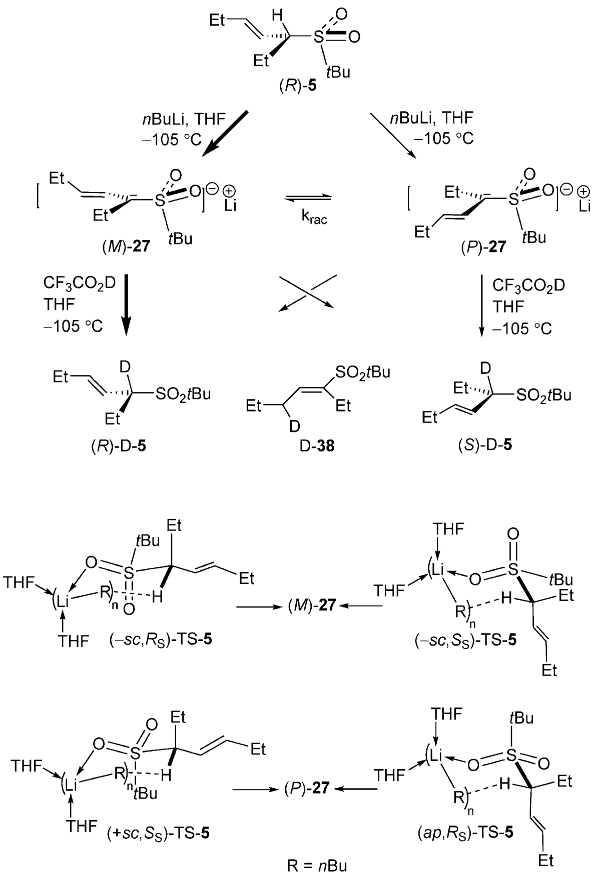
Enantioselective synthesis and electrophilic capture

Deuteration and alkylation

Sulfone (*R*)-**5** was treated with *n*BuLi (1.1 equiv) in THF at −105 °C and after 1 min had elapsed from the beginning of the addition of the base the lithiated carbanion **27** was deuterated at −105 °C with CF_3CO_2D. This sequence led to the formation of a mixture of the allylic sulfone (*R*)-D-**5** (96 % D) of 81 % *ee* and the vinylic sulfone D-**38** (97 % D) in a ratio of 86:14 (Scheme 9). The configuration of the double bond of sulfone D-**38** was not determined. Both reactions were run under standard conditions and special experimental precautions were



Scheme 8. Enantiomerization and isomerisation of the O,C,Li and O,Li CIPs of **26** (L = THF) via solvent assisted topomerisation of the Li atom.



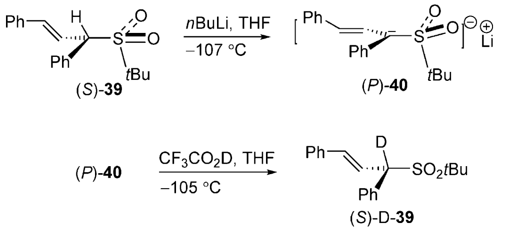
Scheme 9. Enantioselective deprotonation of sulfone (*S*)-**13** and enantioselective deuteration of carbanion (*M*)-**27**.

taken to ensure that both reactions were conducted at −105 °C. Deprotonation of (*R*)-**5** and deuteration of the lithiated carbanion **27** were complete within less than 15 s at −105 °C, the time of addition of the base and the deuteration reagent. The results show that both deprotonation and deuteration had occurred with high enantioselectivities and proceeded with over-all retention of configuration. The isolation of sulfone (*R*)-D-**5** of 81 % *ee* starting from (*R*)-**5** of 94 % *ee* implies that both the deprotonation of (*R*)-**5** and deuteration of the lithiated carbanion **27** had occurred with calculated selectivities of, for example, 93 % *ee*. Based on our previous results of the deprotonation of chiral phenyl-alkyl and dialkyl substituted sulfones,[7,15–17,19,20] deprotonation of the (*R*)-configured sulfone (*R*)-**5** with *n*BuLi had given the lithiated carbanion (*M*)-**27**, the deuteration of which at C1 had occurred from the direction *anti* to the *tert*-butyl group and afforded sulfone (*R*)-D-**5** (Scheme 9). Phenyl-alkyl and dialkyl-substituted *S*-*tert*-butyl and *S*-trifluoromethyl α-sulfonyl carbanions also undergo a highly selective *anti* attack by electrophiles.[7,15–17,19,20] Of the possible CIPs of (*M*)-**27**, the O,Li CIP (*M*)-**27 K** should be more reactive than the O,C,Li CIP (*R*,*R*)-**27 A** (cf. Figure 7), because of the lack of steric hindrance and the negative charge at C1 lowering Li atom.

We had proposed six-membered cyclic transition states (TSs) for the enantioselective deprotonation of chiral benzylic sulfones with RLi.[19,20] The TS models are based on the assumption of an intramolecular deprotonation, following complex formation between the sulfone and *n*BuLi, either as monomer, dimer or tetramer.[57] The developing negative charge of the TS is stabilized by factors which also stabilize the carbanion, including 1) coulombic interaction between the negative charge at C1 and the positively charged S atom, 2) negative hyperconjugation n_C–σ^*_{StBu}[18,20,58–60] and 3) benzylic conjugation. Destabilizing factors are mainly steric interactions around the C1–S bond and 1,3-diaxial interactions. Based on these premises transition states (−*sc*,*R*$_S$)-TS-**5**, (−*sc*,*S*$_S$)-TS-**5**, (+*sc*,*S*$_S$)-TS-**5** and (*ap*,*R*$_S$)-TS-**5** are envisioned for the deprotonation of the allylic sulfone (*R*)-**5**, which are all stabilized by coulombic interaction and allylic conjugation. However, (−*sc*,*R*$_S$)-TS-**5** and (−*sc*,*S*$_S$)-TS-**5**, which both lead to the formation of (*M*)-**27**, should be preferred over (+*sc*,*S*$_S$)-TS-**5** and (*ap*,*R*$_S$)-TS-**5**, which both afford (*P*)-**27**. While (−*sc*,*R*$_S$)-TS-**5** and (−*sc*,*S*$_S$)-TS-**5** experience an additional stabilization by n_C–σ^*_{StBu} interaction, (+*sc*,*S*$_S$)-TS-**5** and (*ap*,*R*$_S$)-TS-**5** lack this extra stabilization. The n_C–σ^*_{SO} interaction in (+*sc*,*S*$_S$)-TS-**5** and (*ap*,*R*$_S$)-TS-**5** should be less efficient than the n_C–σ^*_{StBu} interaction.[18,20] Furthermore, (+*sc*,*S*$_S$)-TS-**5** and (*ap*,*R*$_S$)-TS-**5** are destabilized by 1,3-interaction between the *t*Bu group and a THF molecule.

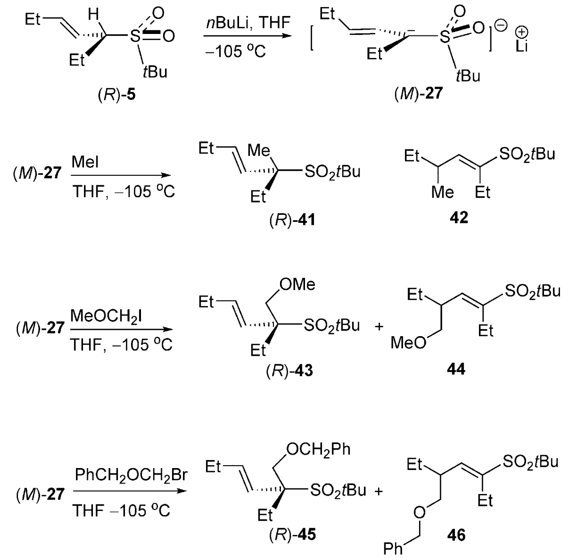
We had previously used time-dependent deuteration of chiral dialkyl and alkyl-phenyl substituted α-sulfonyl carbanions for the determination of the dynamic parameters of racemization.[19,20] In order to determine the racemization dynamics of (*M*)-**27** by time-dependent deuteration, the successive deprotonation of sulfone (*R*)-**5** of 94% *ee* and deuteration of the thus generated carbanion (*M*)-**27** after increasing delay time with formation of sulfone (*R*)-D-**5** were studied. The *ee*-value of (*R*)-D-**5** is a function of (1) the selectivity of the deprotonation of sulfone (*R*)-**5**, (2) the selectivity of the deuteration of carbanion (*M*)-**27** and (3) of the racemization of the carbanion. A series of deprotonation-deuteration experiments was run, in which all experimental parameters, including those of deprotonation and deuteration, were kept constant except the time which elapsed after the addition of *n*BuLi to the sulfone and the beginning of the addition of CF_3CO_2D to the lithiated carbanion, the racemization time t_{rac}. Six deprotonation-deuteration experiments were carried out starting with sulfone (*R*)-**5** (94% *ee*) in THF at −105 °C under variation of t_{rac} from 1 min to 10 min under otherwise identical conditions. The *ee* values of (*R*)-D-**5** (97% to 99% D) were determined by GC analysis on a chiral stationary phase, which also served to prove the (*R*) configuration of the deuterated sulfone by comparison with the starting sulfone. From the slope of the linear plot of ln *ee* versus t_{rac} the rate constant $k_{rac} = 2\times10^{-3}\,s^{-1}$ was estimated and the activation free energy at 168 K was calculated with the aid of the Eyring equation to $\Delta G^{\neq}_{rac} = 12.5 \pm 0.2\,kcal\,mol^{-1}$, which translates to a calculated half-life time of racemization of (*M*)-**27** to $t_{1/2} = 12$ min at −105 °C.

Previously, by time-dependent deuteration a racemization barrier of $\Delta G^{\neq}_{rac} = 12.1 \pm 0.2\,kcal\,mol^{-1}$ (166 K) had been determined for the lithiated allylic-benzylic α-sulfonyl carbanion (*P*)-**40** (Scheme 10).[7] Deprotonation of sulfone (*S*)-**39** (93% *ee*) with *n*BuLi in THF at −105 °C had afforded carbanion (*P*)-**40**, the deuteration of which at −107 °C with CF_3CO_2D (5 equiv) after $t_{rac} = 1$ min had yielded sulfone (*S*)-D-**39** (≥98% D) of 81% *ee*.[7] Thus, not only the deprotonation of sulfones (*S*)-**13** and (*S*)-**39** but also the deuteration of carbanions (*M*)-**27** and (*P*)-**40** take the same stereochemical course and all four reactions are highly enantioselective.



Scheme 10. Synthesis and deuteration of the lithiated carbanion (*P*)-**40**.[7]

The enantioselective synthesis of (*M*)-**27** from sulfone (*R*)-**5** with *n*BuLi provided the basis for a study of the reactivity of the carbanion towards C-electrophiles. Deprotonation of sulfone (*R*)-**5** of 94% *ee* with *n*BuLi (1.1 equiv) in THF at −105 °C with formation of (*M*)-**27** followed by the successive addition first of MeI (5.0 equiv) after 1 min and then of CF_3CO_2D after 2 min led to a mixture of 73% of the deuterated allylic sulfone (*R*)-D-**5** of 73% *ee*, 23% of the deuterated vinylic sulfone D-**38** and 19% of the methylated allylic sulfone (*R*)-**41** of 73% *ee* (Scheme 11, Table 7). The composition of the mixture was determined by ^{1}H NMR spectroscopy and the *ee* values were determined by GC on a chiral stationary phase. Formation of the methylated vinylic sulfone **42** was not detected. The extension of the methylation time to 10 min gave 53% of the methylated sulfone (*R*)-**41** with 64% *ee*. Finally, after a methylation time of 60 min sulfone (*R*)-**41** of 30% *ee* was isolated in 98% yield. Thus, the reactivity of (*M*)-**27** towards MeI is not high enough to successfully compete with its racemization.



Scheme 11. Reactions of carbanion (*M*)-**24** with C-electrophiles in THF at −105 °C.

The reactivity of (*M*)-**27** towards methoxymethyl iodide was much higher than towards MeI. Treatment of sulfone (*R*)-**5** of 94% *ee* with *n*BuLi (1.1 equiv) in THF at −105 °C for 1 min followed by the addition of methoxymethyl iodide (5.0 equiv) after 5 min and then of CF_3CO_2D after a reaction time of only 1 min gave a mixture composed of 86% of the alkylated allylic sulfone (*R*)-**43** of 86% *ee* and 14% of the alkylated vinylic sulfone **44** of 34% *ee* in 91% yield.

Carbanion (*M*)-**27** displayed towards benzoxymethyl bromide a similar high reactivity as towards methoxymethyl iodide. Thus, treatment of sulfone (*R*)-**5** of 94% *ee* with *n*BuLi (1.1 equiv) in THF at −105 °C followed by the addition of $PhCH_2OCH_2Br$ (5.0 equiv) after 5 min and then of CF_3CO_2D after

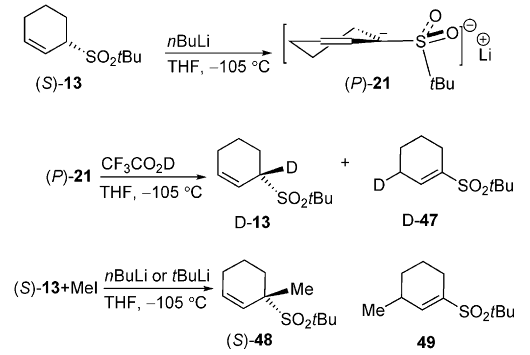
Table 7. Methylation of carbanion (*M*)-**27** with MeI in THF at −105 °C.

t_{rac} [min]	(*R*)-D-**5**/D-**38** [%]	((*R*)-D-**5**) *ee* [%]	(*R*)-**41** [%]	((*R*)-**41** *ee* [%]
2	55:23	73	19	73
10	27:14	67	53	64
60	0:2	–	98	30

5 min gave in 65 % yield a mixture composed of 93 % of the alkylated allylic sulfone (*R*)-**45** of 69 % *ee* and of 7 % of the alkylated vinylic sulfone **46**.

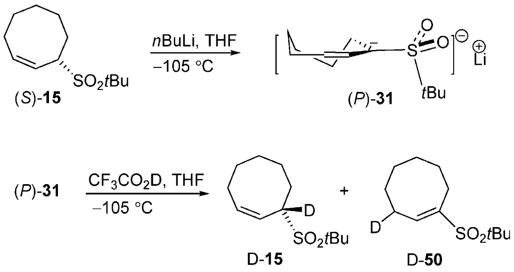
It is interesting to note that the α/γ-selectivity of the reaction of carbanion (*M*)-**27** with methyl iodide was much higher than of the reactions with the more reactive electrophiles CF_3CO_2D, methoxymethyl iodide and benzoxymethyl bromide. The double bond of the vinylic sulfone **44** has the (*E*) configuration. NOE experiments of **44** revealed correlations between 2-H and *t*Bu and between 3-H and the CH_2 group at C1. Based on this result the vinylic sulfone **46** was also assigned the (*E*) configuration. Formation of the (*E*) configured vinylic sulfones is a consequence of the higher reactivity of (*M*)-**27** as compared to its *s-cis* isomer. The configurations of the stereogenic C atoms of **44** and **46** were not determined.

Information about the configurational stability of the six-membered cyclic carbanion (*P*)-**21** could not be gained by DNMR spectroscopy. Thus, deprotonation-deuteration experiments starting with sulfone (*S*)-**13** of 96 % *ee* were carried out. Sulfone (*S*)-**13** was treated with *n*BuLi (1.1 equiv) in THF at −105 °C and after 1 min carbanion (*P*)-**21** was deuterated at −105 °C with CF_3CO_2D (5 equiv), which gave a mixture of the allylic sulfone D-**13**, the vinylic sulfone D-**47** and sulfone (*S*)-**13** in a ratio of 82:11:7 (Scheme 12). The mixture of D-**13** and (*S*)-**13** had an *ee* value of only 15 %. This result is compatible either with a low configurational stability of the lithiated carbanion or with a low enantioselectivity of deprotonation. In order to differentiate between the two possibilities, "external" and "internal" trapping experiments[17,61] of carbanion (*P*)-**21** with methyl iodide were carried out. In the "external" trapping experiment sulfone (*S*)-**13** was treated with *n*BuLi (1.1 equiv) in THF at −105 °C and after $t_{rac}=5$ min had elapsed methyl iodide was added to carbanion (*P*)-**21** at low temperature. Then the mixture was kept for 15 min at low temperatures, warmed to 0 °C and quenched with CF_3CO_2D. This procedure gave the racemic sulfone *rac*-**48** in 99 % yield. Formation of the vinylic sulfone **49** was not observed. A similar "external" trapping experiment of (*P*)-**21** starting with sulfone (*S*)-**13** except that t_{rac} was only 1 min also afforded *rac*-**48** in 98 % yield. In the "internal" trapping experiment *n*BuLi (1.1 equiv) was added to a mixture of sulfone (*S*)-**13** and methyl iodide (4 equiv) in THF at −105 °C. After the mixture was kept at low temperature for 15 min, it was quenched at 0 °C with CF_3CO_2D. This experiment gave the methylated sulfone (*S)*-**48** with 62 % *ee* in 99 % yield. The use of *t*BuLi in the deprotonation-methylation of sulfone (*S*)-**13** under otherwise identical conditions afforded sulfone (*S)*-**48** with 59 % *ee* in 98 % yield. The trapping experiments of (*P*)-**21** with methyl iodide indicate that the lithiated carbanion (*P*)-**21** has a low configurational stability, which is the major cause for the medium overall selectivity in the deprotonation-deuteration experiments starting with the cyclic allylic sulfone (*S*)-**13**. The experiments with *n*BuLi and *t*BuLi show that the enantioselectivity of the deprotonation does not depend on RLi as previously observed in the case of the deprotonation of alkyl-substituted benzylic *tert*-butyl sulfones. Although the configurations of sulfones (*R*)-**41**, (*R*)-**43**, (*R*)-**45** and (*S*)-**48** were not determined, the tertiary sulfones were assigned the (*R*) and (*S*) configurations, respectively, on the basis of the sterochemical course of the deuteration of carbanion (*M*)-**27**. Previous studies of the deuteration and alkylation of dialkyl- and alkyl-phenyl-substituted chiral α-sulfonyl carbanions had shown that both reactions always take the same stereochemical course.[15–17,19,20]



Scheme 12. Synthesis and reactions of carbanion (*P*)-**21** in THF at −105 °C.

The deprotonation of the eight-membered cyclic sulfone (*S*)-**15** of ≥ 98 % *ee* with *n*BuLi was much slower than that of the six-membered cyclic sulfone (*S*)-**13**. For example, treatment of (*S*)-**15** with *n*BuLi (1.2 equiv) in THF at −105 °C and the subsequent deuteration of the carbanion (*P*)-**31** with CF_3CO_2D at −105 °C after $t_{rac}=1$ min gave a mixture consisting of sulfone D-**15**, the vinylic sulfone D-**50** and (*S*)-**15** in a ratio of 15:23:62 in 98 % yield (Scheme 13). The mixture of D-**15** and (*S*)-**15** had an *ee* value of 79 %. In a second experiment sulfone (*S*)-**15** ≥98 % *ee*) was treated with *t*BuLi (1.5 equiv) in THF at −85 °C and after $t_{rac}=3$ min carbanion (*P*)-**31** was deuterated with CF_3CO_2D at −105 °C. This sequence afforded a mixture of sulfone D-**15** of only 20 % *ee* together with D-**50** in a ratio of 73:27 in 98 % yield.



Scheme 13. Synthesis and deuteration of carbanion (*P*)-**31** in THF at −105 °C.

Conclusions

Lithiated alkyl substituted allylic *S-tert*-butyl α-sulfonyl carbanions are configurationally stable at low temperatures at the time scale of their reactions with reactive electrophiles. Their configurational stability is lower than that of dialkyl and alkyl-aryl substituted *S-tert*-butyl α-sulfonyl carbanions. Lithiated alkyl substituted allylic *S-tert*-butyl α-sulfonyl carbanions can be obtained with high enantioselectivity through reaction of the corresponding enantiopure allylic sulfones with organolithiums and their reactions with reactive electrophiles are highly enantioselective. The two-step sequence of deprotonation and electrophilic capture proceeds with retention of configuration. Deuteration and alkylation of the alkyl substituted *S-tert*-butyl allylic α-sulfonyl carbanions are only of medium regioselectivity. Although they have not been studied yet the reaction of lithiated allylic *S-tert*-butyl α-sulfonyl carbanions with aldehydes will be the most interesting ones. NMR spectroscopy, cryoscopy, ab initio calculation and X-ray crystal structure analyses all suggest that lithiated allylic α-sulfonyl carbanions form monomeric and dimeric CIPs in THF solution. The monomeric CIPs have either O-Li and C1-Li bonds or only O-Li and are in rapid equilibrium even at low temperatures. The anions preferentially adopt the *s-trans* conformation around the C1-C2 bond, have nearly planar allylic units, the typical C1–S conformation and are stabilized by allylic conjugation, Coulomb interaction and n_{C1}–σ^{*}_{SR} hyperconjugation. The n_c–σ^*_{SR} interaction (negative hyperconjugation) and allylic conjugation are the stereoelectronic effects, which determine the conformations of the lithiated allylic α-sulfonyl carbanions around the C1-S and C1-C2 bonds. These two effects are also responsible for the conformations of the lithiated benzylic α-sulfonyl carbanions around the C1–S and C1–Ci bonds.

The O,Li CIPs of type **K** should exhibit a higher reactivity towards electrophiles than the O,C,Li CIPs of type **A** due to the lack of a C1 bonded Li atom.

Experimental Section

Experimental details

All reactions were carried out in absolute solvents under argon in oven-dried and argon filled glassware by using Schlenk, cannula and syringe techniques. Tetrahydrofuran (THF) was filtered through alumina and distilled from potassium/benzophenone under argon. Methyl iodide was distilled from CaH_2 under argon. [D$_8$]THF was distilled from potassium in a micro solvent still under argon. Diglyme was distilled from calcium hydride. $MeOCH_2I$ and (allylsulfonyl)benzene were obtained from commercial sources and $PhCH_2OCH_2Br$[62] was synthesized according to the literature. *n*BuLi (in *n*-hexane) and *t*BuLi (in *n*-pentane) were acquired from commercial sources and were standardized by titration with diphenylacetic acid.[63] *n*Bu^{6}Li in *n*-hexane was synthesized according to the literature.[64] Analytical thin-layer chromatography (TLC) was performed on E. Merck pre-coated TLC plates (silica gel 60 F$_{254}$, layer thickness 0.2 mm). Flash chromatography (denoted as chromatography) was performed with E. Merck silica gel 60 (0.063–0.200 mm). Gas chromatography was done with a Chrompack CP-9000 instrument by using a DB 5 Carlo Erba CP-Sil-8 column: length 30 m, diameter 0.32 mm, film thickness 0.25 μm. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR 300 (300 MHz, 75 MHz), Varian Gemini 300 (300 MHz, 75 MHz), Varian Unity 500 (500 MHz, 125 MHz) and Varian Inova 400 (400 MHz, 100 MHz) instruments. Chemical shifts are reported relative to $SiMe_4$ ($\delta = 0.00$ ppm) $CHCl_3$ ($\delta = 7.24$ ppm, 77.1 ppm) and [D$_8$]THF ($\delta = 1.72$ ppm, 3.58 ppm, 25.3 ppm, 67.2 pm) as internal standards. Splitting patterns in the ^{1}H NMR spectra are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; hept, heptet; m, multiplet; br, broad, vbr, very broad and combinations thereof. Peaks in the ^{13}C NMR spectra are denoted as “u” for carbons with zero or two attached protons and as “d” for carbons with one or three attached protons, as determined from the APT puls sequence. Assignments in the ^{1}H NMR spectra were made by GMQCOSY, GNOE, HETCOR experiments and those in the ^{13}C NMR spectra were made by DEPT experiments. ^{6}Li NMR spectra were run on a Varian Unity 500 (74 MHz) instrument. IR spectra were recorded on a PerkinElmer PE 1760 S FT instrument. Only peaks of $\nu \geq 800$ cm^{-1} are listed, vs = very strong, s = strong, m = medium, w = weak. Low resolutions mass spectra were recorded on a Varian MAT 212 S instrument using electron impact ionization (EI, 70 eV). Only peaks of $m/z \geq 80$ and an intensity of $\geq$ 10%, except decisive ones, are listed. Elemental analyses were performed by the Institute of Organic Chemistry (RWTH Aachen University) micro analytical laboratory with PerkinElmer CHN-analyzer 240C and Heraeus CHN-Rapid analyzer. Optical rotations were measured with a PerkinElmer 241 instrument at approximately 20 °C, $[\alpha]_D$ in (grd × dm^3)/(dm × g) and *c* in (g × dm^{-3}). GC MS analyses: Varian Model 3700, Varian MAT 112 S, EI 70 eV. GC: Chrompack CP-9000, FID. DB-5 (CP-9000): 30 m, 0.32 mm, 0.25 mm, H_2, 60 kPa. Lipodex E (permethyl-β-cyclodextrin): 25 m, 0.25 mm, 15 mm, H_2, 50 kPa. HPLC: Waters 600E system controller, waters 510, (*S*,*S*)-Whelk-01 column. Cryoscopy was performed according to the method,[65] which we had previously also used for lithiated benzylic α-sulfonyl carbanions.[18,20] Single crystals of sulfone (*S*)-**13** were obtained through crystallization from EtOAc/*n*-hexane 1:1 at room temperature.

Computational methods

All calculations were performed with the Gaussian 09 suite of quantum-chemical routines[66] running on the facilities of the IT Center of RWTH Aachen University. Plausible initial structures were defined using standard structural parameters. Specific interactions between the solvent and the lithium compound were modelled by adding two dimethyl ether molecules to each metal atom. The geometries of all species under consideration were then energetically optimized at the MP2 level of ab initio theory employing the 6–31+G* set of basis functions. The stationary points obtained in this way were verified to be local minima by normal mode analyses. In order to get a better description of the bulk solvent effects, additional single point calculations at the optimized geometries of the complexes consisting of the Li compounds and the two ether molecules were performed at the PCM (polarizable continuum model) level[51] of the SCRF method using the dielectric constant for tetrahydrofuran as implemented in Gaussian 09 ($\varepsilon = 7.4257$).

General procedure for the synthesis of lithiated allylic α-sulfonyl carbanions for NMR spectroscopy (GP1)

To a solution of the sulfone (0.30 mmol) in THF (5 mL) at −75 °C was added *n*BuLi (1 equivalent of 1.50 M to 1.60 M in *n*-hexane) or *n*Bu^{6}Li (1 equivalent of 2.00 M in *n*-hexane). After the mixture was stirred for 5 min at low temperatures, the cooling bath was removed and the volatiles were removed in vacuo. The oily residue was dried at room temperature for 20 min in high vacuo. Then the highly viscous residue was dissolved in [D$_8$]THF (0.70 mL) and the solution was transferred via cannula to an oven-dried and argon filled Schlenk-type NMR tube. Then the NMR tube was cooled for 45 s to −75 °C, evacuated for 30 s in high vacuo and sealed with a micro Bunsen burner.

General procedure for the enantioselective synthesis of lithiated allylic α-sulfonyl carbanions and their reactions with electrophiles (GP2)

An oven-dried long-necked Schlenk flask, which was equipped with a Teflon-coated magnetic stirring bar, was filled with argon. The flask was charged with the sulfone and closed with a rubber septum, which was fitted with a thermo-element reaching to 1 cm above the bottom of the flask. The temperature measurements were done with a precision thermometer Kelvimat Typ 4321 (Burster Präzisionsmeßtechnik, Gernsbach, Germany). Then the flask was evacuated three times and refilled with argon, charged with THF and the solution was cooled under argon to the given temperature in a continuously stirred nitrogen/EtOH cooling bath (3 L). Then the long-necked flask was immersed just below the joint into the cooling bath and the solution of RLi was added via film-cooling (the solution was allowed to run down the cooled long neck) to the solution of the sulfone under rapid stirring. The solution of RLi was added at such a rate that an efficient film-cooling was guaranteed. After the given time, the mixture was treated with a solution of the electrophile under rapid stirring and film-cooling. Because of the exothermic reactions, an efficient cooling is required in order to achieve temperature control. Deuteration and quenching of reaction mixture after the time given were carried out with a 2.00 M solution of CF_3CO_2D in THF except otherwise stated. Then ether (20 mL) was added and the mixture was successively washed with saturated aqueous $NaHCO_3$, brine and water. In the case of halogen containing electrophiles the organic phase was also washed with aqueous $Na_2S_2O_3$. The organic phase was dried ($MgSO_4$) and concentrated in vacuo.

Synthesis and characterization

See Supporting Information.

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Keywords: allyl anion · alpha-sulfonyl carbanion · chiral compounds · lithium · reaction mechanisms · structure elucidation

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