

Chiral Fluorinated α -Sulfonyl Carbanions: Enantioselective Synthesis and Electrophilic Capture, Racemization Dynamics, and Structure

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Abstract: Enantiomerically pure trifluorones $R^1CH(R^2)SO_2CF_3$ have been synthesized starting from the corresponding chiral alcohols via thiols and trifluoromethylsulfanes. Key steps of the syntheses of the sulfanes are the photochemical trifluoromethylation of the thiols with CF_3Hal (Hal=halide) or substitution of alkoxyphosphinediamines with CF_3SSCF_3 . The deprotonation of $RCH(Me)SO_2CF_3$ (R = CH_2Ph , $iHex$) with $nBuLi$ with the formation of salts $[RC(Me)-SO_2CF_3]Li$ and their electrophilic capture both occurred with high enantioselectivities. Displacement of the SO_2CF_3 group of (*S*)- $MeOCH_2C(Me)(CH_2Ph)SO_2CF_3$ (95% *ee*) by an ethyl group through the reaction with $AlEt_3$ gave alkane $MeOCH_2C(Me)(CH_2Ph)Et$ of 96% *ee*. Racemization of salts $[R^1C(R^2)SO_2CF_3]Li$ follows first-order kinetics and is mainly an enthalpic process with small negative activation entropy as revealed by polarimetry and dynamic NMR (DNMR) spectroscopy. This is in accordance with a $C_\alpha-S$ bond rotation as the rate-determining step. Lithium α -(*S*)-trifluoromethyl- and α -(*S*)-nona-

fluorobutylsulfonyl carbanion salts have a much higher racemization barrier than the corresponding α -(*S*)-*tert*-butylsulfonyl carbanion salts. Whereas $[PhCH_2C(Me)SO_2tBu]Li/DMPU$ (DMPU = dimethylpropylurea) has a half-life of racemization at $-105^\circ C$ of 2.4 h, that of $[PhCH_2C(Me)SO_2CF_3]Li$ at $-78^\circ C$ is 30 d. DNMR spectroscopy of amides $(PhCH_2)_2NSO_2CF_3$ and $(PhCH_2)N(Ph)SO_2CF_3$ gave N-S rotational barriers that seem to be distinctly higher than those of nonfluorinated sulfonamides. NMR spectroscopy of $[PhCH_2C(Ph)SO_2R]M$ (M = Li, K, NBu_4 ; R = CF_3 , tBu) shows for both salts a confinement of the negative charge mainly to the C_α atom and a significant benzylic stabilization that is weaker in the trifluoromethylsulfonyl carbanion. According to crystal structure analyses, the carbanions of salts $\{[PhCH_2C(Ph)SO_2CF_3]Li \cdot L\}_2$ (L = 2 THF, tetramethylethylenediamine

(TMEDA)) and $[PhCH_2C(Ph)SO_2CF_3]NBu_4$ have the typical chiral $C_\alpha-S$ conformation of α -sulfonyl carbanions, planar C_α atoms, and short $C_\alpha-S$ bonds. Ab initio calculations of $[MeC(Ph)SO_2tBu]^-$ and $[MeC(Ph)SO_2CF_3]^-$ showed for the fluorinated carbanion stronger $n_C \rightarrow \sigma_{S-CF_3}^*$ and $n_O \rightarrow \sigma_{S-CF_3}^*$ interactions and a weaker benzylic stabilization. According to natural bond orbital (NBO) calculations of $[R^1C(R^2)SO_2R]^-$ (R = tBu , CF_3) the $n_C \rightarrow \sigma_{S-R}^*$ interaction is much stronger for R = CF_3 . Ab initio calculations gave for $[MeC(Ph)SO_2tBu]Li \cdot 2 Me_2O$ an O,Li, C_α contact ion pair (CIP) and for $[MeC(Ph)SO_2CF_3]Li \cdot 2 Me_2O$ an O,Li,O CIP. According to cryoscopy, $[PhCH_2C(Ph)SO_2CF_3]Li$, $[iHexC(Me)SO_2CF_3]Li$, and $[PhCH_2C(Ph)SO_2CF_3]NBu_4$ predominantly form monomers in tetrahydrofuran (THF) at $-108^\circ C$. The NMR spectroscopic data of salts $[R^1(R^2)SO_2R^3]Li$ ($R^3 = tBu$, CF_3) indicate that the dominating monomeric CIPs are devoid of $C_\alpha-Li$ bonds.

Keywords: ab initio calculations • carbanions • chirality • racemization • sulfone

Introduction

The structure and dynamics of chiral carbanions have aroused much attention because of the importance they have gained in asymmetric synthesis.^[1] In particular, the fac-

tors that determine the configurational stability of chiral carbanions are topics of key interest.^[1,2] We had synthesized chiral lithium (*S*)-*tert*-butylsulfonyl carbanion salts of type **I** (Figure 1) and studied their structure and racemization dynamics.^[3,4] The salts predominantly form monomeric and di-

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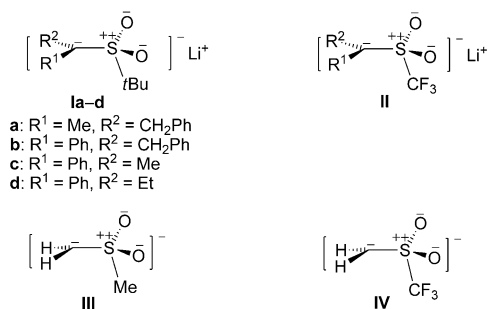


Figure 1. Chiral and achiral α -(*S*)-*tert*-butyl- and α -(*S*)-trifluoromethylsulfonyl carbanions.

meric O–Li contact ion pairs (CIPs) in solution in tetrahydrofuran (THF) and in the crystal phase. The rate-determining step of the racemization of **I** is the rotation around the C_α–S bond, the barrier of which is mainly governed by the steric effects exerted by the substituents at the C_α and S atoms and the n_C→σ*_{S–tBu} interaction (negative hyperconjugation). Although the enantiomerically pure salts **I** could be synthesized from the corresponding chiral sulfones and captured with electrophiles with high enantioselectivities, they are configurationally stable only at –100 °C for a relatively short period of time. Therefore, it was desirable to see whether chiral α -sulfonyl carbanion salts can be devised that are endowed with a higher configurational stability for further studies and future synthetic applications. We had previously obtained preliminary experimental evidence that suggested that the corresponding lithium (*S*)-trifluoromethylsulfonyl carbanion salts **II** have a higher configurational stability than the (*S*)-*tert*-butylsulfonyl carbanion salts **I**.^[5] The experimental observations were supported by ab initio calculations of the achiral α -sulfonyl carbanions **III** and **IV**, which showed that the fluorinated carbanion has a higher C_α–S rotational barrier because of the stronger n_C→σ*_{S–CF₃} interaction.^[6] These findings together with a significantly lower basicity^[7] and nucleophilicity^[8] indicated a possible general uniqueness of (*S*)-trifluoromethylsulfonyl carbanions. Although the last two features have been known for decades, their origin is not fully understood despite several imaginative investigations.^[9,10] The corresponding (*S*)-trifluoromethylsulfones (triflones) also occupy a special place among sulfones, mainly because of the trifluoromethylsulfonyl group, which is one of the strongest neutral electron-acceptor groups known.^[11] Triflones have gained importance as functional materials,^[12a,b] bioactive compounds,^[12c,g,h] ligands,^[12e,f] CF₃[–]-transfer reagents,^[12d,i,j] and solvents for nuclear-waste treatment.^[12k]

In this paper, we give a detailed account of our experimental and theoretical studies of the synthesis and electrophilic capture, dynamics, electronic, and ion-pair structure of the chiral (*S*)-trifluoromethylsulfonyl carbanion salts **II** and the corresponding (*S*)-nonafluorobutylsulfonyl carbanion salts.^[13] It will be shown that salts **II** 1) generally have a distinctly higher racemization barrier than the corresponding α -(*S*)-*tert*-butylsulfonyl carbanion salts **I**, 2) can be syn-

thesized in enantiomerically pure form, 3) are configurationally stable for rather long periods of time at –78 °C, 4) capture electrophiles with high stereoselectivities, and 5) significantly differ in their electronic structure from the corresponding α -(*S*)-butylsulfonyl carbanion salts.^[14]

Results and Discussion

Synthesis of achiral and racemic (*S*)-trifluoromethyl- and (*S*)-nonafluorobutylsulfones: Because of our previous studies of the (*S*)-*tert*-butylsulfonyl carbanion salts **Ia–d**,^[3,4] we selected the (*S*)-trifluoromethylsulfonyl carbanion salts **1**, **2**,

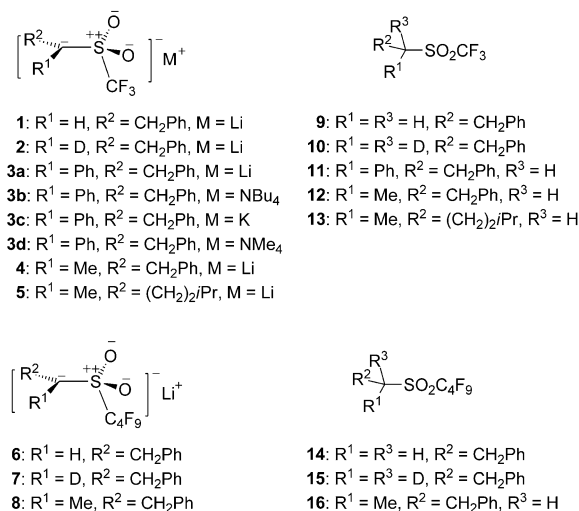
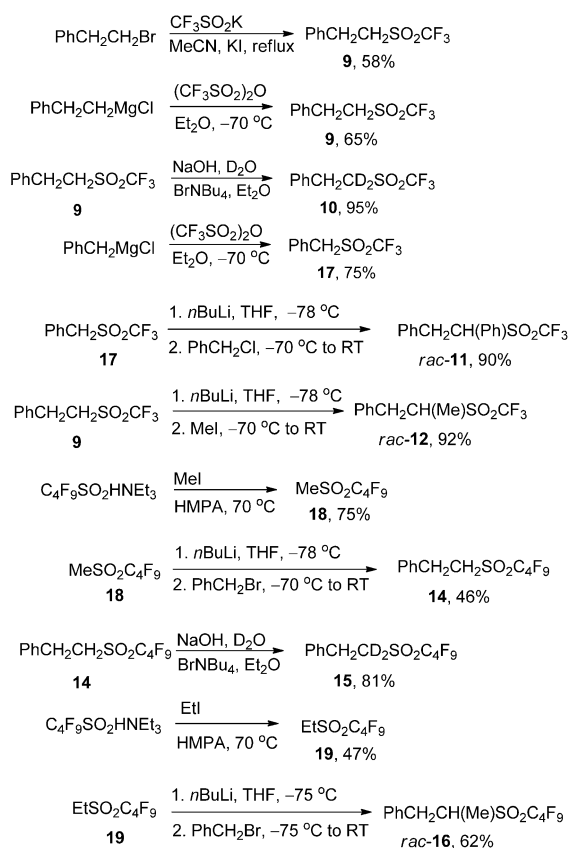


Figure 2. α -(*S*)-Trifluoromethyl- and α -(*S*)-nonafluorobutylsulfonyl carbanion salts, (*S*)-trifluoromethylsulfones, and (*S*)-nonafluorobutylsulfones.

3a–d, **4**, and **5** (Figure 2) for the determination of 1) the configurational stability of salts of type **II** and its dependence on the counterion and substituents at the C_α atom, and 2) the study of the enantioselective synthesis and electrophilic capture of **II**. The nonafluorobutylsulfonyl salts **6**, **7**, and **8** were also included in the investigation to probe the influence of the size of the fluoroalkyl group at the S atom upon the configurational stability. The enantiomerically pure triflones (*S*)-**12**, (*R*)-**12**, and (*S*)-**13**, the racemic (*S*)-fluoroalkylsulfones *rac*-**11**, *rac*-**12**, and *rac*-**16**, and the achiral (*S*)-fluoroalkylsulfones **9**, **10**, **14**, and **15** were required for the planned studies.

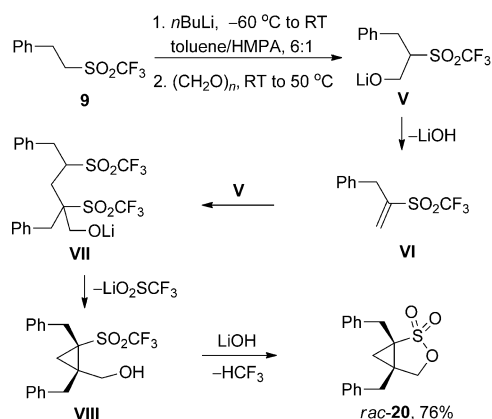
Triflones **9**, **10**, *rac*-**11**, and *rac*-**12**, and nonafluorobutylsulfones **14**, **15**, and *rac*-**16** were synthesized as outlined in Scheme 1. Triflone **9** was prepared in 58% yield upon treatment of PhCH₂CH₂Br with CF₃SO₂K^[15,16] in MeCN in the presence of KI. The availability of (CF₃SO₂)₂O from commercial sources led us to also prepare triflone **9** from PhCH₂CH₂MgCl and (CF₃SO₂)₂O in 65% yield. Deuteration of triflone **9** with NaOH/D₂O under phase-transfer conditions afforded the bis-deuterated triflone **10** (≥ 195% D) in 95% yield. The treatment of PhCH₂MgCl with



Scheme 1. Synthesis of achiral and racemic triflones and nonafluorobutyl-sulfones.

(CF_3SO_2) $_2\text{O}$ gave triflone **17** in 75% yield,^[17] the successive reactions of which with *n*BuLi and PhCH_2Cl finally furnished the racemic triflone *rac*-**11** in 90% yield. The successive treatment of triflone **9** with *n*BuLi and MeI gave the racemic triflone *rac*-**12** in 92% yield. The methylation of salt $\text{C}_4\text{F}_9\text{SO}_2\text{HNEt}_3$ with MeI in hexamethylphosphotriamide (HMPA) afforded nonafluorobutylsulfone **18** in 75% yield,^[18] the successive treatment of which with *n*BuLi and PhCH_2Br gave nonafluorobutylsulfone **14** in 46% yield. Deuterium labeling of nonafluorobutylsulfone **14** under phase-transfer conditions afforded the bis-deuterated nonafluorobutylsulfone **15** ($\geq 195\%$ D) in 81% yield. Finally, the alkylation of $\text{C}_4\text{F}_9\text{SO}_2\text{HNEt}_3$ with EtI in HMPA furnished nonafluorobutylsulfone **19** in 47% yield, the successive treatment of which with *n*BuLi and PhCH_2Br gave the racemic nonafluorobutylsulfone *rac*-**16** in 62% yield.

Surprisingly, the successive treatment of triflone **9** with 1 equiv of *n*BuLi in toluene/HMPA and paraformaldehyde did not give the corresponding α -hydroxymethyl derivative as expected but afforded the racemic sultone *rac*-**20** in 76% yield (Scheme 2). The mode of the unprecedented formation of sultone *rac*-**20**,^[19] which has a bicyclo[3.1.0]hexane skeleton, is not clear at present. The sequence that led to *rac*-**20** most likely started with the deprotonation of triflone **9** and reaction of the corresponding α -(*S*)-trifluoromethylsulfonyl carbanion with formaldehyde under formation of the lithium



Scheme 2. Synthesis of the bicyclic sultone *rac*-**20** via putative intermediates **V**–**VIII**.

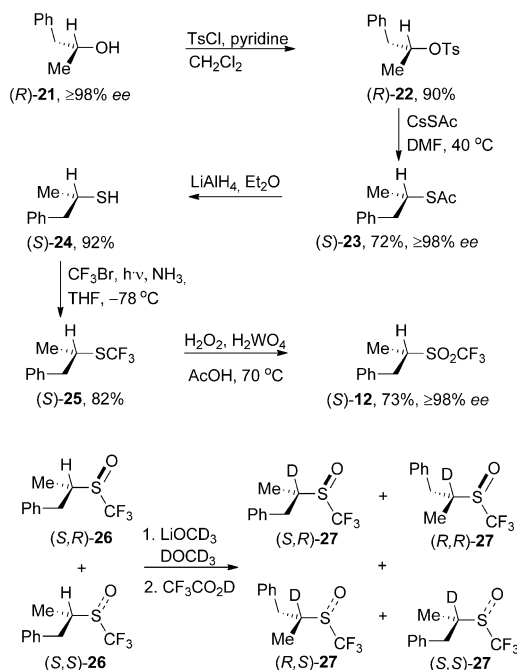
alcoholate **V**. The alcoholate perhaps suffered transmetalation and elimination of LiOH and gave the vinyl triflone **VI**. Michael reaction of **VI** with the transmetalated alcoholate **V** could have afforded the bis-triflone **VII**, which perhaps underwent transmetalation and cyclization under elimination of LiO_2SCF_3 and gave the cyclopropane derivative **VIII**. Finally, base-induced cyclization of hydroxytriflone **VIII** yielded the sultone. In principle, the key steps of Scheme 2, the Michael reaction of the vinyl triflone,^[8] cyclization of the bis-triflone to the cyclopropane,^[8c,16] and substitution of the CF_3 group of the triflone by the hydroxyl group^[20] have all been exemplified.

Synthesis of enantiomerically pure (*S*)-trifluoromethylsul-

fones: The synthesis of the enantiomerically pure (*S*)-*tert*-butylsulfones, which served as starting materials for the enantioselective synthesis of **I**, had been accomplished either by means of an $\text{S}_{\text{N}}2$ reaction of the corresponding chiral-activated secondary alcohols with $\text{MS}t\text{Bu}$ or through chromatographic resolution of the racemic sulfones.^[3] The synthesis of the enantiomerically pure triflones by means of a similar $\text{S}_{\text{N}}2$ reaction of the corresponding activated chiral secondary alcohols with MSO_2CF_3 is not feasible because of the low nucleophilicity of triflinate salts.^[8a-c,1] In fact, when we started with our investigation of salts **II**, enantioselective syntheses of secondary triflones of type **11**, **12**, and **13** and the reaction of MSO_2CF_3 with nonactivated secondary alkylating reagents had not been described. Thus, we developed two routes to the enantiomerically pure secondary triflones **12** and **13** from chiral secondary alcohols through the corresponding (*S*)-trifluoromethylsulfanes. The key step of the first route is the establishment of the $\text{S}-\text{CF}_3$ through application of the known photochemical substitution of CF_3Br or CF_3I with thiols under formation of the corresponding trifluoromethylsulfanes.^[21,22] The second route features as key step the generation of the $\text{C}-\text{S}$ bond through the substitution of alkoxyphosphinediamines with CF_3SSCF_3 under formation of the trifluoromethylsulfanes.^[23a] Although the substitution of alkoxyphosphinediamines with CF_3SSCF_3 had been described, its stereochemical course was not known.

Both routes are based on the corresponding chiral secondary alcohols as starting materials and are concluded by the racemization free oxidation of the trifluoromethylsulfanes to the corresponding triflones by using $\text{H}_2\text{O}_2/\text{H}_2\text{WO}_4$ and $\text{NaIO}_4/\text{RuCl}_3$ ^[24] as oxidants.

The first route to the triflones used alcohol (*R*)-**21** as starting material, which was obtained enantiomerically pure in high yield through a lipase-catalyzed kinetic resolution of the corresponding racemic chloroacetate (Scheme 3).^[25] To-

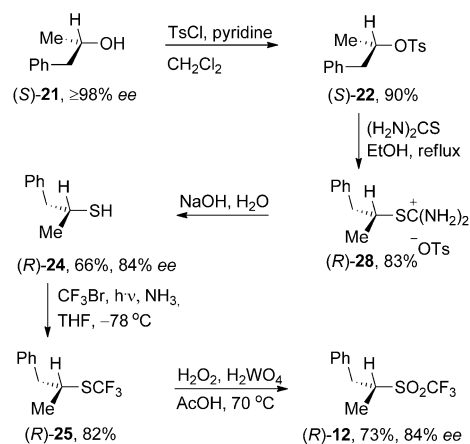


Scheme 3. Enantioselective synthesis of triflone (*S*)-**12** via thioacetate (*S*)-**23**.

sylation of (*R*)-**21** gave tosylate (*R*)-**22** in 90% yield. Treatment of (*R*)-**22** with CsSAc in dimethylformamide (DMF) afforded the thioacetate (*S*)-**23** of $\geq 98\%$ ee (GC) in 72% yield. Reduction of (*S*)-**23** with LiAlH_4 furnished thiol (*S*)-**24**^[26] in 92% yield. Photolysis of a mixture of thiol (*S*)-**24** and CF_3Br at -78°C in a low-temperature photolysis apparatus (see the Supporting Information) proceeded rapidly and efficiently and gave sulfane (*S*)-**25** in 82% yield. Oxidation of sulfane (*S*)-**25** with H_2O_2 in the presence of H_2WO_4 afforded triflone (*S*)-**12** of $\geq 98\%$ ee in 73% yield. At first the ee value of (*S*)-**12** was determined in an indirect manner at the stage of the sulfoxides (*S,R*)-**26** and (*S,S*)-**26** as follows. The oxidation of (*S*)-**25** was terminated at approximately 60% conversion and a mixture of sulfoxides (*S,R*)-**26** and (*S,S*)-**26** was isolated by chromatography in addition to triflone (*S*)-**12**. The successive treatment of the mixture of (*S,R*)-**26** and (*S,S*)-**26** with $\text{LiOCD}_3/\text{DOCD}_3$ and $\text{CF}_3\text{CO}_2\text{D}$ gave a mixture of the deuterated isomers (*S,R*)-**27**, (*R,S*)-**27**, (*S,S*)-**27**, and (*R,R*)-**27**, the composition of which could be determined by ^1H NMR spectroscopy in CDCl_3 in the presence of $[\text{Eu}(\text{hfc})_3]$ (50 mol %; $\text{hfc} = \text{tris}[3\text{-}(\text{heptafluoropropyl})\text{hydroxymethylene}]\text{-D-camphorate}$). A similar analysis of

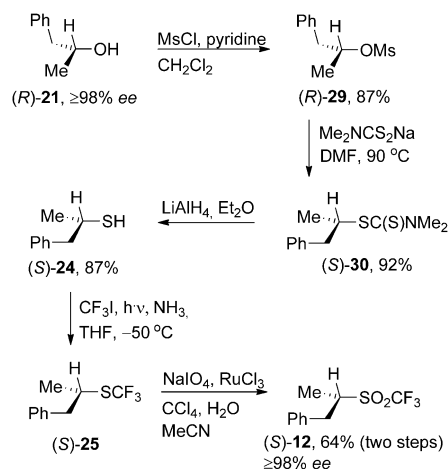
the starting mixture of (*S,R*)-**26** and (*S,S*)-**26** showed both to be of $\geq 98\%$ ee. In later synthetic runs it was found that the ee value of triflone (*S*)-**12** could be more directly determined by GC analysis on chiral stationary phases.

The synthesis of (*S*)-**12** required a careful chromatographic purification at the stage of thioacetate (*S*)-**23**. Therefore, in the synthesis of the enantiomeric triflone (*R*)-**12** from the enantiomeric alcohol (*R*)-**21**, which is also accessible enantiomerically pure in high yield through the lipase-catalyzed kinetic resolution of the racemic chloroacetate,^[25] thiourea was used in the substitution of tosylate (*S*)-**22** (Scheme 4) in



Scheme 4. Enantioselective synthesis of triflone (*R*)-**12** via isothiuronium salt (*R*)-**28**.

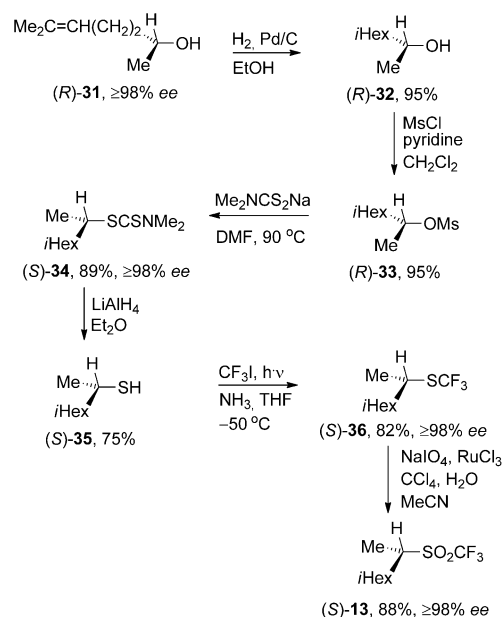
the hopes of a purification of the isothiuronium salt by crystallization. Cleavage of the thus obtained crystalline isothiuronium salt (*R*)-**28** gave thiol (*R*)-**24**, which had, however, an ee value of only 84% according to GC analysis. Finally, thiol (*R*)-**24** was converted by means of sulfane (*R*)-**25** to triflone (*R*)-**12** of 84% ee. To optimize the crucial substitution of the enantiomerically pure alcohol derivative, the alternative route depicted in Scheme 5 was followed in the



Scheme 5. Enantioselective synthesis of triflone (*S*)-**12** via carbamodithioate (*S*)-**30**.

synthesis of (*S*)-**12** by using a different sulfur nucleophile. Mesylation of alcohol (*R*)-**21** of $\geq 98\%$ *ee* afforded mesylate (*R*)-**29** in 87% yield. The treatment of mesylate (*R*)-**29** with $\text{Me}_2\text{NCS}_2\text{Na}$ gave carbamodithioate (*S*)-**30** in 92% yield. The reduction of (*S*)-**30** with LiAlH_4 furnished thiol (*S*)-**24** of $\geq 98\%$ *ee* (GC), which was converted via sulfane (*S*)-**25** to triflone (*S*)-**12** of $\geq 98\%$ *ee* (GC) in 64% overall yield on the basis of (*S*)-**30**. Because of analytical reasons, *rac*-**12** was also synthesized following Scheme 5.

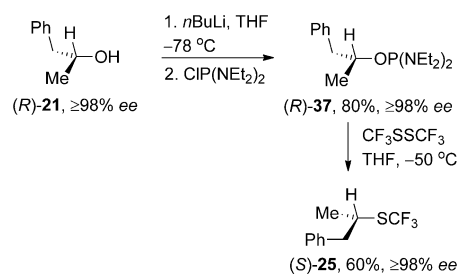
Finally, the dialkyl-substituted triflone (*S*)-**13** was synthesized (Scheme 6). The enantiomerically pure unsaturated al-



Scheme 6. Enantioselective synthesis of triflone (*S*)-**13**.

cohol (*R*)-**31** was readily available through a kinetic resolution of the corresponding racemic chloroacetate by using immobilized *Candida antarctica* lipase (48%, $\geq 98\%$ *ee*) instead of the previously applied *Pseudomonas cepacia* lipase, which gives the *S*-configured alcohol (*S*)-**31**.^[27] Hydrogenation of (*R*)-**31** afforded the saturated alcohol (*R*)-**32** of $\geq 98\%$ *ee* in 95% yield. Mesylation of alcohol (*R*)-**32** furnished mesylate (*R*)-**33** in 95% yield. The treatment of (*R*)-**33** with $\text{Me}_2\text{NCS}_2\text{Na}$ gave carbamodithioate (*S*)-**34** of $\geq 98\%$ *ee* (GC) in 85% yield. Thiol (*S*)-**35** was obtained in 75% yield through reduction of (*S*)-**34** with LiAlH_4 . The photochemical trifluoromethylation of thiol (*S*)-**35** with CF_3I proceeded efficiently and gave sulfane (*R*)-**36** of $\geq 98\%$ *ee* (GC) in 82% yield. Oxidation of sulfane (*S*)-**36** with $\text{NaIO}_4/\text{RuCl}_3$ furnished triflone (*S*)-**13** of $\geq 98\%$ *ee* (GC) in 88% yield.

The second route to triflones used in this study involves a substitution of an activated alkoxyphosphinediamine with the in situ generated anion F_3CS^- and was realized by using alcohol (*R*)-**21** (Scheme 7) as the starting material. The successive treatment of alcohol (*R*)-**21** with *n*BuLi and $\text{CIP}(\text{NEt}_2)_3$ in THF at low temperatures afforded the alkoxy-



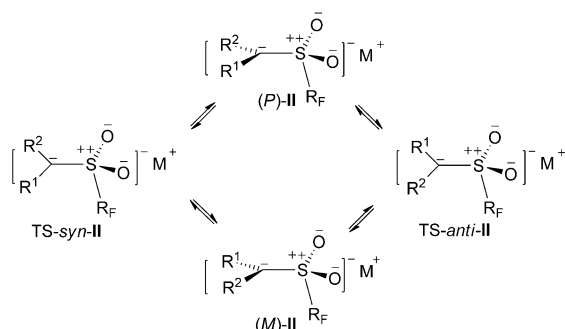
Scheme 7. Synthesis of trifluoromethylsulfane (*S*)-**25** from phosphinediamine (*R*)-**37**.

phosphinediamine (*R*)-**37** of $\geq 98\%$ *ee* (GC) in 80% yield. The reaction of the air- and moisture-sensitive phosphinediamine (*R*)-**37** with CF_3SSCF_3 gave sulfane (*S*)-**30** of $\geq 98\%$ *ee* in 60% yield. Thus, the substitution of (*R*)-**37** proceeded with complete inversion of the configuration. However, the formation of several side products was observed in the substitution of (*R*)-**37**, the complete separation of which from the sulfane was too difficult. Thus, the synthesis of triflone (*S*)-**12** from alcohol (*R*)-**21** by this route was carried out without isolation of the sulfane. For analytical reasons (*S*)-**37**, *rac*-**37**, (*R*)-**25**, and *rac*-**25** were also synthesized following Scheme 7.

The syntheses of the enantiomerically pure triflones described above show that both the photochemical trifluoromethylation of the dialkyl-substituted thiols and the oxidation of the corresponding trifluoromethylsulfanes proceeded without racemization. Of the two routes to chiral triflones followed in this work, the one by means of the photochemical trifluoromethylation of chiral thiols with commercially available CF_3I and CF_3Br is preferred. Although CF_3SSCF_3 is also commercially available, the disulfane is highly toxic^[23b] and only half of it is used in the alkoxyphosphinediamine route. Chiral thiols and (*S*)-acyl thiols are readily accessible by several routes including $\text{S}_\text{N}2$ reaction of activated chiral alcohols,^[28] lipase-catalyzed kinetic resolution of racemic thioacetates,^[29,30a,b] palladium-catalyzed enantioselective substitution of racemic allylic carbonates^[31a] and rearrangement of racemic allylic carbamothioates,^[31b-d] and organocatalytic kinetic resolution of racemic thiols.^[32] Preliminary investigations indicate that aryl- and alkyl-substituted trifluoromethylsulfanes should also be accessible through the photochemical trifluoromethylation of the corresponding thiols.^[30b,c] However, the oxidation of the aryl- and alkyl-substituted trifluoromethylsulfanes to the corresponding triflones seems to be less facile than that of the dialkyl-substituted trifluoromethylsulfanes.^[30b,c]

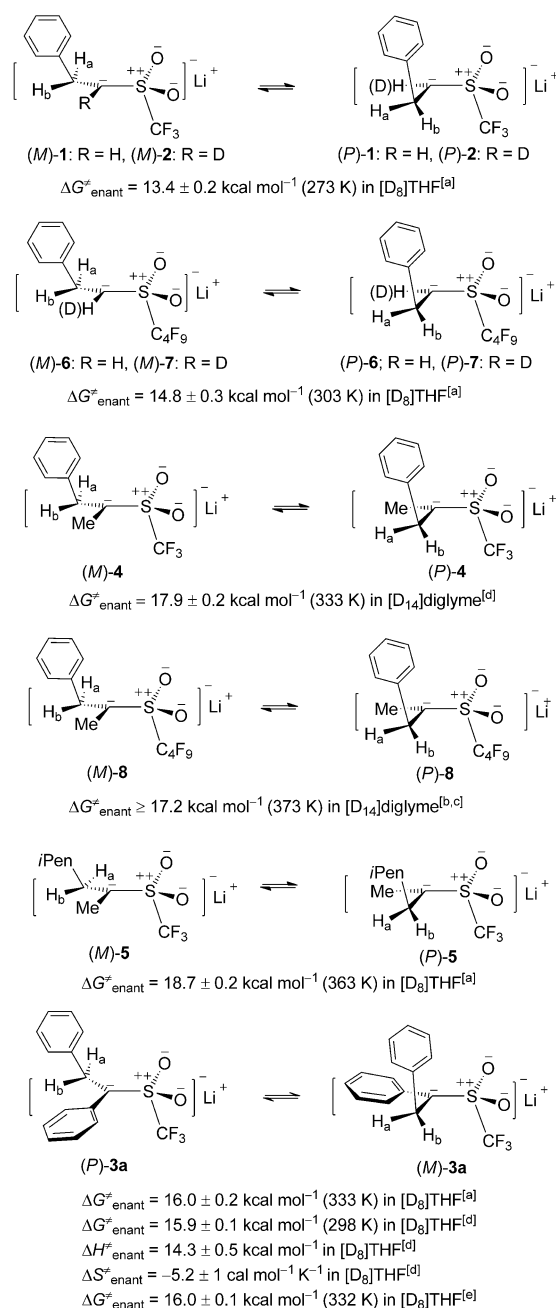
Estimation of the enantiomerization barriers of racemic (*S*)-trifluoromethyl- and (*S*)-nonafluorobutylsulfonyl carbanion salts by dynamic NMR (DNMR) spectroscopy: The lithium salts *rac*-**1**, *rac*-**2**, *rac*-**3a**, *rac*-**4**, *rac*-**5**, *rac*-**6**, *rac*-**7**, and *rac*-**8** were prepared from the corresponding fluoroalkylsulfones **9**, **10**, *rac*-**11**, *rac*-**12**, *rac*-**13**, **14**, **15**, and *rac*-**16** with *n*BuLi and *n*PrLi, respectively, in THF, and removal of the solvent

under high vacuum. The ammonium salts *rac*-**3b** and *rac*-**3d** were obtained upon treatment of triflone *rac*-**11** with R₄NOH (R = Bu, Me) in ether/*i*PrOH, removal of the volatiles under high vacuum, and recrystallization from *n*-hexane/THF. The potassium salt *rac*-**3c** was prepared from *rac*-**11** and KN(SiMe₃)₂ in ether and removal of the volatiles under high vacuum. Solutions of the salts in [D₈]THF, [D₆]DMSO (DMSO = dimethylsulfoxide), and [D₁₄]diglyme (diglyme = diethyleneglycoldimethylether) were sealed in NMR spectroscopy tubes. In all cases, the ¹H NMR spectra of salts *rac*-**1**, *rac*-**2**, *rac*-**3a**, *rac*-**3b**, *rac*-**3c**, *rac*-**3d**, *rac*-**5**, *rac*-**6**, and *rac*-**7** showed temperature-dependent reversible coalescence phenomena for the signals of the diastereotopic protons of the methylene group attached to the C_α atom. The activation free energy for the enantiomerization of the salts at the coalescence temperature was estimated^[33] on the basis of the assumption that it follows first-order kinetics (see below). Enantiomerization of (*P*)-**II** to (*M*)-**II** has to involve inter alia a C_α-S bond rotation. The rotation can in principle occur by means of transition states TS-*syn*-**II** and TS-*anti*-**II**, the energies of which are generally different (Scheme 8). DNMR spectroscopy only allows a determination of the lower barrier.



Scheme 8. Enantiomerization of α -(*S*)-fluoroalkylsulfonyl carbanion salts (priority: R¹ > R²) (coordination geometry of the C_α atoms is not considered).

DNMR spectroscopy of the monoalkyl-substituted salt *rac*-**1**, which carries an (*S*)-trifluoromethyl group, in [D₈]THF under selective decoupling of the H atom at the C_α atom gave an estimated enantiomerization barrier $\Delta G_{\text{enant}}^{\ddagger} = (13.4 \pm 0.2) \text{ kcal mol}^{-1}$ at the coalescence temperature of 273 K (Scheme 9). The same result was obtained for the corresponding deuterated salt *rac*-**2**. DNMR spectroscopy of the monoalkyl-substituted salt *rac*-**6**, the S atom of which bears a nonafluorobutyl group, in [D₈]THF under selective decoupling of the H atom at the C_α atom gave an estimated enantiomerization barrier $\Delta G_{\text{enant}}^{\ddagger} = (14.8 \pm 0.3) \text{ kcal mol}^{-1}$ at the coalescence temperature of 303 K. DNMR spectroscopy of the corresponding deuterated salt *rac*-**7** gave the same results. The enantiomerization barriers of the dialkyl-substituted salts *rac*-**4** and *rac*-**8**, which bear a trifluoromethyl- and nonafluorobutyl group, respectively, at the S atom in [D₈]THF could not be estimated by the coalescence temperature method because of the too-low boiling point of



[a] Estimated at the coalescence temperature. [b] Coalescence was not observed. [c] Decomposition at 373 K. [d] Line-shape analysis. [e] Calculated.

Scheme 9. Thermodynamic parameters of the enantiomerization of lithium α -(*S*)-trifluoromethyl- and α -(*S*)-nonafluorobutylsulfonyl carbanion salts.

the solvent. However, line-shape analysis^[34] of the signal of the CH₂ group of *rac*-**4** in [D₁₄]diglyme at 333 K gave an activation free energy $\Delta G_{\text{enant}}^{\ddagger} = (17.9 \pm 0.2) \text{ kcal mol}^{-1}$. Because of a coalescence temperature for *rac*-**8** of $\geq 373 \text{ K}$, the activation free energy $\Delta G_{\text{enant}}^{\ddagger}$ of this salt has to be $\geq 17.2 \text{ kcal mol}^{-1}$. DNMR spectroscopy of *rac*-**5** in [D₈]THF under selective decoupling of the H atoms at the α position to the methylene group at the C_α atom gave an estimated barrier $\Delta G_{\text{enant}}^{\ddagger} = (18.7 \pm 0.2) \text{ kcal mol}^{-1}$ at the coalescence tempera-

ture of 363 K. Finally, the enantiomerization of the alkyl-substituted benzylic (*S*)-trifluoromethylsulfonyl carbanion salt *rac*-**3a** was investigated. DNMR spectroscopy of *rac*-**3a**, which was prepared using crystalline (*M/P*)-**3a**·4 THF (see below), in $[D_8]$ THF gave an estimated barrier $\Delta G_{\text{enant}}^{\ddagger} = (16.0 \pm 0.2) \text{ kcal mol}^{-1}$ at the coalescence temperature of 333 K. To obtain the other thermodynamic parameters of *rac*-**3a**, fourteen $^1\text{H NMR}$ spectra were recorded in the temperature range of -21 to 142°C . Line-shape analysis of eight spectra (signal(s) of the methylene group) in the temperature range of -21.4 to 92.0°C was performed. Only values of the exchange rate constant k_{enant} between 33.9 and 92°C were considered for their analysis because in this temperature range the most significant alterations of the line shape occurred. An analysis of the Eyring plot (Figure 3)

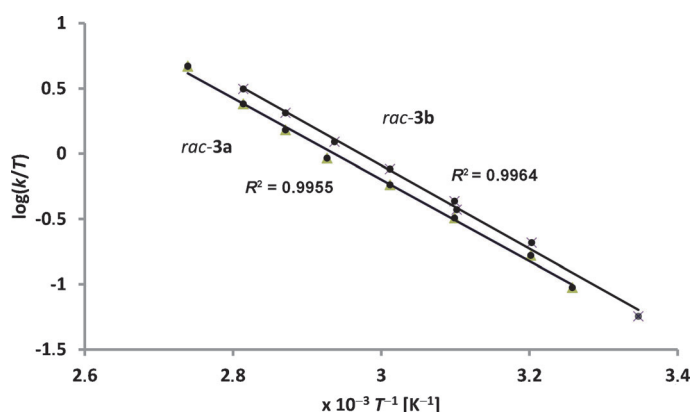
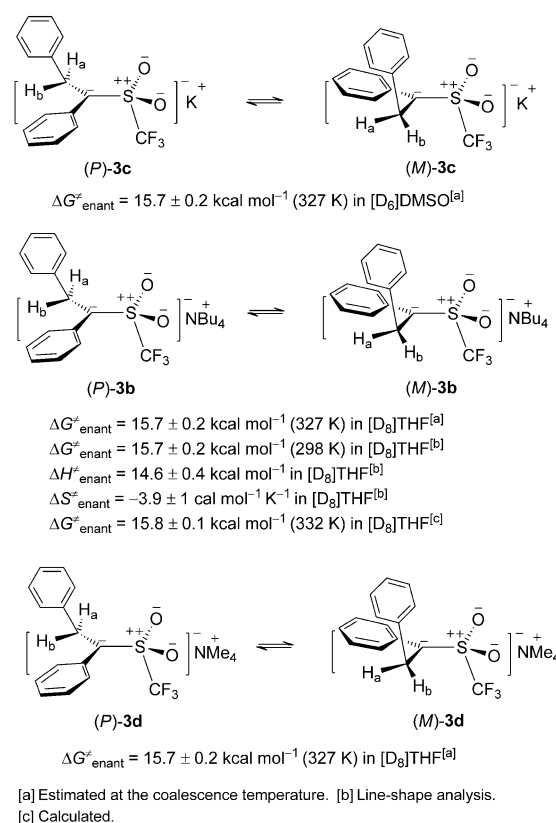


Figure 3. Eyring plot of the line-shape analysis derived exchange rates (k) of the enantiomerization of salts *rac*-**3a** and *rac*-**3b** in $[D_8]$ THF as a function of the temperature.

gave the equation $\log(k_{\text{enant}}/T) = -3128/T + 9.19$ and the thermodynamic parameters $\Delta G_{\text{enant}}^{\ddagger} = (15.9 \pm 0.1) \text{ kcal mol}^{-1}$, $\Delta H_{\text{enant}}^{\ddagger} = (14.3 \pm 0.5) \text{ kcal mol}^{-1}$, and $\Delta S_{\text{enant}}^{\ddagger} = (-5.2 \pm 1) \text{ cal mol}^{-1} \text{ K}^{-1}$.

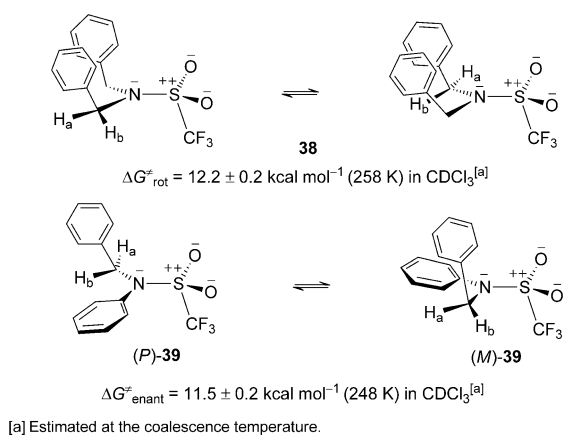
For the determination of the influence of the counterion and thus the ion pairing upon reaching the enantiomerization barrier, the potassium salt *rac*-**3c**, tetrabutylammonium salt *rac*-**3b**, and tetramethylammonium salt *rac*-**3d** were also studied (Scheme 10). DNMR spectroscopy of *rac*-**3c** in $[D_6]$ DMSO gave an estimated barrier $\Delta G_{\text{enant}}^{\ddagger} = (15.7 \pm 0.2) \text{ kcal mol}^{-1}$ at the coalescence temperature of 327 K, whereas that of *rac*-**3b** and *rac*-**3d** in $[D_8]$ THF also furnished for both ammonium salts an estimated barrier $\Delta G_{\text{enant}}^{\ddagger} = (15.7 \pm 0.2) \text{ kcal mol}^{-1}$ at the coalescence temperature of 327 K. To obtain the other thermodynamic parameters of *rac*-**3b**, twelve $^1\text{H NMR}$ spectra (signal(s) of the methylene group) were recorded in the temperature range of -21.4 to 100.2°C . Line-shape analysis of the spectra in the temperature range of -21.4 to 100.2°C was performed. Only values of the exchange rate constant k_{enant} between 25.6 to 82.2°C were considered for their analysis. An analysis of the Eyring plot (see Figure 3) gave the equation $\log(k_{\text{enant}}/T) = -3186/T + 9.47$ and the thermodynamic parameters $\Delta G_{\text{enant}}^{\ddagger}(298) =$



Scheme 10. Thermodynamic parameters of the enantiomerization of potassium and tetraalkylammonium α -(*S*)-trifluoromethylsulfonyl carbanion salts.

$(15.7 \pm 0.2) \text{ kcal mol}^{-1}$, $\Delta H_{\text{enant}}^{\ddagger} = (14.6 \pm 0.4) \text{ kcal mol}^{-1}$, and $\Delta S_{\text{enant}}^{\ddagger} = (-3.9 \pm 1) \text{ cal mol}^{-1} \text{ K}^{-1}$.

(*S*)-Trifluoromethylsulfonamides are isoelectronic to α -(*S*)-trifluoromethylsulfonyl carbanions and preferentially adopt an N–S conformation, which is similar to the C_{α} –S conformation of the carbanions.^[35a,b] It was therefore of interest to determine the rotational barrier of *N,N*-disubstituted (*S*)-trifluoromethylsulfonamides, the N–S bond of which seems to be shorter than the C_{α} –S bond of disubstituted (*S*)-trifluoromethylsulfonyl carbanions (see below).^[35a,b] (*S*)-Trifluoromethylsulfonamides are of interest because of their incorporation in chiral ligands^[35c,d,e] and as biological active compounds.^[35f] Despite the relevance of (*S*)-trifluoromethylsulfonamides, information about their N–S rotational barrier is scarce. DNMR spectroscopy of 1,3,5-tris(trifluoromethylsulfonyl)-1,3,5-triazinane and 1-(methylsulfonyl)-3,5-bis(trifluoromethylsulfonyl)-1,3,5-triazinane had given activation barriers for N–S rotation of $\Delta G_{\text{rot}}^{\ddagger} = 13.0 \text{ kcal mol}^{-1}$ (263 K, CD_3CN)^[36a] and $\Delta G_{\text{rot}}^{\ddagger} = 13.5 \text{ kcal mol}^{-1}$ (283 K, $(\text{CD}_3)_2\text{CO}$)^[36b] respectively. DNMR spectroscopy of the acyclic trifluoromethylsulfonamides **38** and *rac*-**39** in CDCl_3 furnished estimated rotation barriers of $\Delta G_{\text{rot}}^{\ddagger} = (12.2 \pm 0.2) \text{ kcal mol}^{-1}$ at the coalescence temperature of 258 K and $\Delta G_{\text{rot}}^{\ddagger} = (11.5 \pm 0.2) \text{ kcal mol}^{-1}$ at the coalescence temperature of 248 K, respectively (Scheme 11).^[37] Thus, the rotational barrier of sulfonamide *rac*-**39** is $3.9 \text{ kcal mol}^{-1}$ lower than that

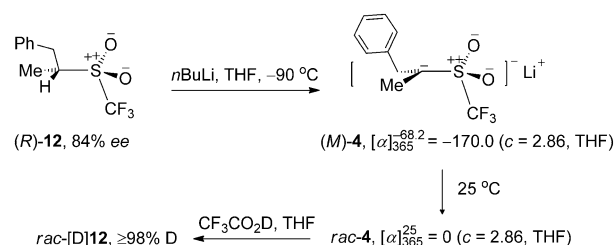


Scheme 11. Thermodynamic parameters of the N–S rotation of trifluoromethylsulfonamides.

of the corresponding lithium salt *rac*-**3a** ($\Delta G_{\text{enant}}^{\ddagger} = (15.4 \pm 0.2) \text{ kcal mol}^{-1}$ at 258 K), the carbanion of which is isoelectronic to *rac*-**39**. For the nonafluorobutylsulfonamide $(\text{PhCH}_2)_2\text{NSO}_2\text{C}_4\text{F}_9$ and heptadecafluorooctylsulfonamide $\text{Et}_2\text{NSO}_2\text{C}_8\text{F}_{17}$, DNMR spectroscopy had yielded activation barriers for N–S rotation of $\Delta G_{\text{rot}}^{\ddagger} = (14.9 \pm 0.8) \text{ kcal mol}^{-1}$ (298 K, CDCl_3)^[36c] and $\Delta G_{\text{rot}}^{\ddagger} = 15.3 \text{ kcal mol}^{-1}$ (309 K, $(\text{CD}_3)_2\text{CO}$)^[36d] respectively. Although a direct comparison of the rotational barriers of the trifluoromethylsulfonamide **38** and nonafluorobutylsulfonamide $(\text{PhCH}_2)_2\text{NSO}_2\text{C}_4\text{F}_9$ is not possible, the higher barrier of the latter sulfonamide points to a significant steric contribution to the N–S rotational barrier. Unfortunately, information about the N–S rotational barriers of the corresponding (*S*)-alkyl(aryl)sulfonamides and (*S*)-*tert*-butylsulfonamides are lacking.^[36c,38] Thus, a quantification of the effect of the F atoms upon the rotational barrier of sulfonamides is not possible. It seems, however, that (*S*)-fluoroalkylsulfonamides have a higher rotational barrier than the nonfluorinated sulfonamides, perhaps because of the larger steric effects exerted by the CF_3 , C_4F_9 , and C_8F_{17} groups in connection with the shorter N–S bonds^[35a,b,36c] and a stronger $n_{\text{N}} \rightarrow \sigma_{\text{S-RF}}^*$ interaction.^[36b,c,37]

Determination of the racemization barriers of nonracemic lithium (*S*)-trifluoromethylsulfonyl carbanion salts by polarimetry: DNMR spectroscopy of salts *rac*-**1**, *rac*-**2**, *rac*-**3a**, *rac*-**3b**, *rac*-**3c**, *rac*-**3d**, *rac*-**4**, *rac*-**5**, *rac*-**6**, *rac*-**7**, and *rac*-**8** yielded estimated free energies of activation for their enantiomerization. Ultimately, DNMR spectroscopy of salts *rac*-**3a** and *rac*-**3b**, which carry an aryl and alkyl group at the C_α atom, all gave thermodynamic parameters of enantiomerization. According to these parameters, the fluorinated salts have, as expected, a significantly higher configurational stability than the *α*-*tert*-butylsulfonyl carbanion salts **I**. Therefore, the enantioselective synthesis of the chiral (*S*)-trifluoromethylsulfonyl carbanion salts (*M*)-**4** and (*P*)-**5**, both of which carry two alkyl groups at the C_α atom, was attempted and their racemization kinetics studied by two different

methods: directly by polarimetry and indirectly by time-dependent deuteration.^[4] Salt (*M*)-**4** was selected for the polarimetric experiments at low temperatures. The reaction of triflone (*R*)-**12** ($\geq 98\% ee$) with *n*BuLi in THF at -90°C was enantioselective and gave the nonracemic *M*-configured lithium salt (*M*)-**4**, which has an optical rotation of $[\alpha]_{365}^{68.2} = -170.0$ ($c = 2.86$, THF) (Scheme 12). The optical rotation



Scheme 12. Synthesis of salt (*M*)-**4** from triflone (*R*)-**12**.

fell to zero within 20 min at 25°C , and quenching of the solution of the salt with $\text{CF}_3\text{CO}_2\text{D}$ furnished the racemic triflone *rac*-[D]**12** with a D content of $\geq 98\%$ in practically quantitative yield.

Racemization of (*M*)-**4** in THF was polarimetrically monitored at -33.9°C as a function of time by using the low-temperature tube described previously.^[4] Salt (*M*)-**4** was prepared from triflone (*R*)-**12** ($\geq 98\% ee$) and *n*BuLi in THF at -95°C and the solution of the salt was rapidly transferred to the tube by means of a thermo-isolated syringe. The temperature of the solution of (*M*)-**4** in THF was internally measured with a digital thermometer. A plot of $\ln(\alpha_t/\alpha_0)$ versus t for the salt showed a good linearity over 6.5 half-lives (Figure 4), the linearity of which indicated that racemi-

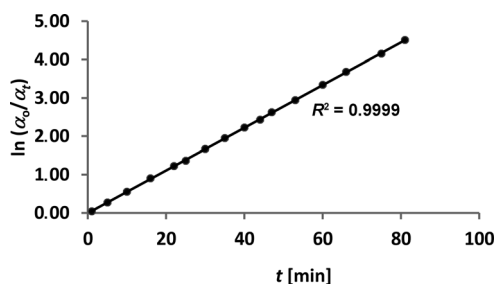
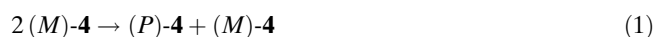


Figure 4. Racemization of salt (*M*)-**4** in THF at -33.9°C and $c = 0.12 \text{ mol L}^{-1}$.

zation follows first-order kinetics and the existence of a linear relationship between $[\alpha]$ and the concentration of (*M*)-**4**. The macroscopically observable process of racemization is regarded as the irreversible transformation of the optically active species into the racemate according to Equation (1). The time dependence of the optical rotation is described by Equation (2).



$$\ln(\alpha_o/\alpha_t) = -k_{\text{rac}}t \quad (2)$$

From the slope of the plot $\ln(\alpha_o/\alpha_t)$ versus t , the rate constant for racemization $k_{\text{rac}} = (9.27 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$ at 239 K was deduced. The half-life for racemization of $(M)\text{-4}$ is $\tau_{1/2\text{rac}} = (12.5 \pm 0.6) \text{ min}$ at 239 K. The Eyring equation gave an activation free energy $\Delta G_{\text{rac}}^\ddagger = (17.2 \pm 0.1) \text{ kcal mol}^{-1}$ for the racemization at 239 K. The lithium (S) -trifluoromethylsulfonyl carbanion salts *rac*-**3a** and *rac*-**5** exist in THF at -108°C to more than 90% as monomers (see below). The DNMR experiments revealed that the counterion and the solvent have only a minor influence on the enantiomerization barrier (see above). Starting from the determination of the racemization of $(M)\text{-4}$ at -33.9°C and $c = 0.12 \text{ mol L}^{-1}$, further measurements at lower concentrations were run to further prove this notion (Figure 5 and Table 1). Plots of

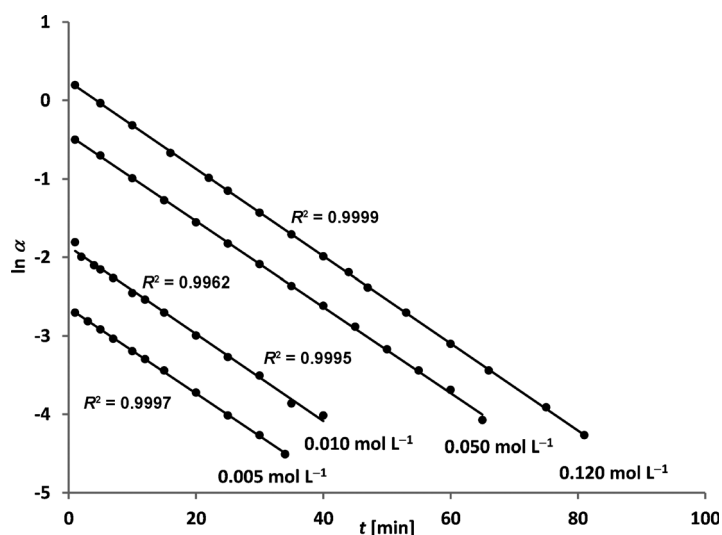


Figure 5. Polarimetric investigation of the racemization of salt $(M)\text{-4}$ at various concentrations ($T = -33.9^\circ\text{C}$, $\lambda = 546 \text{ nm}$).

Table 1. Rate constants and half-lives of the racemization of salt $(M)\text{-4}$ at various concentrations and -33.9°C .

$c \text{ [mol L}^{-1}]$	$k_{\text{rac}} \times 10^{-4} \text{ [s}^{-1}]$	$\tau_{1/2} \text{ [min]}$	$t/\tau_{1/2}$
0.120	9.27 ± 0.4	12.5 ± 0.6	6.5
0.050	9.04 ± 0.4	12.8 ± 0.6	5.1
0.010	8.99 ± 0.5	12.8 ± 0.7	3.1
0.005	9.07 ± 0.4	12.7 ± 0.6	2.7

$\ln \alpha$ versus t not only showed good linearity for the four different concentrations but also good parallelism of the lines. This proves that in the concentration range investigated there is no noticeable influence of the concentration on the rate.

We had previously found that the addition of 4 equiv of dimethylpropylurea (DMPU) to the (S) -*tert*-butylsulfonyl

carbanion salt $(P)\text{-Ia}$ in THF enhanced its configurational stability.^[4] Replacement of THF molecules of $(P)\text{-Ia} \cdot (\text{THF})_m$ by DMPU molecules perhaps leads to the formation of a CIP of type $(P)\text{-Ia} \cdot (\text{THF})_n(\text{DMPU})_o$, which has a higher racemization barrier because of the bulky DMPU ligands, which sterically hinder the rotation around the $\text{C}_\alpha\text{-S}$ bond more than the THF ligands. On the basis of this result the influence of DMPU upon the enantiomerization barrier of $(M)\text{-4} \cdot (\text{THF})_m$ was investigated. Following the racemization of $(M)\text{-4}$ in the presence of 4 equiv of DMPU for 4 half-lives gave the linear dependency between $\ln(\alpha_o/\alpha_t)$ and t shown in Figure 6. Thus, racemization of $(M)\text{-4} \cdot (\text{THF})_n(\text{DMPU})_o$ also follows first-order kinetics. For a direct comparison, Figure 7 shows plots of $\ln(\alpha_o/\alpha_t)$ versus t for the

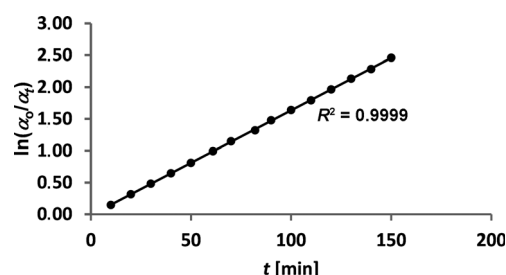


Figure 6. Racemization of salt $(M)\text{-4}$ in the presence of DMPU (4 equiv) in THF at -33.9°C and at $c = 0.05 \text{ mol L}^{-1}$.

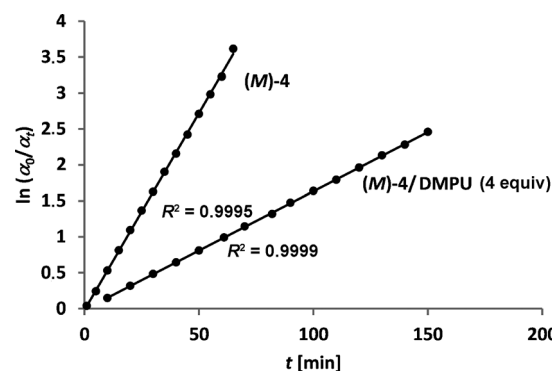


Figure 7. Comparison of the racemization of salts $(M)\text{-4}$ and $(M)\text{-4/DMPU}$ (4 equiv of DMPU) in THF.

racemization of $(M)\text{-4} \cdot (\text{THF})_m$ and $(M)\text{-4} \cdot (\text{THF})_n(\text{DMPU})_o$. A comparison of the kinetic parameters of both salts (Table 2) shows that the half-life, $\tau_{1/2}$, of $(M)\text{-4} \cdot (\text{THF})_n(\text{DMPU})_o$ is greater by a factor of 3.3 than that of $(M)\text{-4} \cdot (\text{THF})_m$.

Table 2. Kinetic and thermodynamic parameters of the racemization of salt $(M)\text{-4}$ in THF at -33.9°C .

Solvent	$k_{\text{rac}} \times 10^{-4} \text{ [s}^{-1}]$	$\tau_{1/2\text{rac}} \text{ [min]}$	$\Delta G_{\text{rac}}^\ddagger \text{ [kcal mol}^{-1}]$
THF/DMPU ^[a]	2.88	42.0	17.7 ± 0.1
THF	9.04	12.8	17.2 ± 0.1

[a] 4 equivalents of DMPU.

Racemization of (*M*)-**4** in THF at $c=0.05\text{M}$ was polarimetrically monitored ($\lambda=546\text{nm}$)^[4] at five different temperatures as a function of time. Salt (*M*)-**4** was prepared from triflone (*R*)-**12** ($\geq 98\%$ *ee*) and *n*BuLi in THF at -95°C , and the solution of the salt was rapidly transferred to the tube by means of a thermo-isolated syringe. The temperature of the solution of salt (*M*)-**4** in THF was internally measured with a digital thermometer ($\pm 0.3\text{K}$). The rate constants k_{rac} listed in Table 3 are average values of three

Table 3. Temperature dependency of the rate constant of the racemization of salt (*M*)-**4** in THF.

T [$^\circ\text{C}$]	T^{-1} [K^{-1}]	k_{rac} [s^{-1}]	$\tau_{1/2}$ [min]	$\log(k/T)$
-23.7	4.008×10^{-3}	4.00×10^{-3}	2.8	-4.795
-28.8	4.092×10^{-3}	1.99×10^{-3}	5.5	-5.089
-33.9	4.179×10^{-3}	9.39×10^{-4}	12.8	-5.406
-38.8	4.266×10^{-3}	4.18×10^{-4}	30.4	-5.749
-43.7	4.357×10^{-3}	2.03×10^{-4}	56.9	-6.054

separate measurements. After each measurement *rac*-**4** was deuterated with $\text{CF}_3\text{CO}_2\text{D}$ to ensure that no protonation of (*M*)-**4** had occurred during the experiment. An Eyring plot of $\log(k_{\text{rac}}/T)$ versus $1/T$ showed a good linearity (Figure 8). Analysis of the Eyring plot gave the equation $\log(k_{\text{rac}}/T) =$

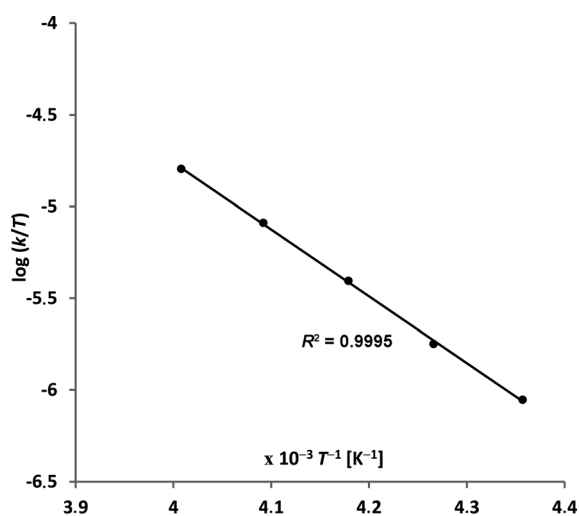


Figure 8. Eyring plot of the racemization of salt (*M*)-**4**.

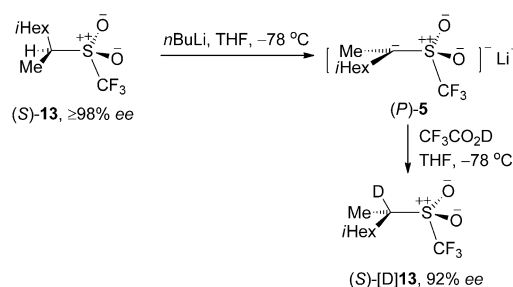
$-3663/T + 9.90$ and calculation furnished the activation parameter $\Delta H_{\text{rac}}^\ddagger = (16.7 \pm 0.3)\text{kcal mol}^{-1}$, $\Delta S_{\text{rac}}^\ddagger = (-1.9 \pm 1.1)\text{cal mol}^{-1}\text{K}^{-1}$, and $\Delta G_{\text{rac}}^\ddagger = (17.3 \pm 0.3)\text{kcal mol}^{-1}$ at 298K . Calculation gave the racemization barrier $\Delta G_{\text{rac}}^\ddagger = (17.2 \pm 0.1)\text{kcal mol}^{-1}$ at -33.9°C , the value of which remained constant within the error range in the temperature interval between -23.7 and -43.7°C . Calculation of the extrapolated half-life of racemization of (*M*)-**4** at -78°C gave $\tau_{1/2\text{rac}} = 30\text{d}$. This value of $\tau_{1/2\text{rac}}$ shows the exceptional configurational stability of (*M*)-**4**. In an experiment, the optical rotation of (*M*)-**4** in THF was measured at -87.5°C , which

remained constant for the measurement time of 3 h. Then the solution of (*M*)-**4** was warmed to -78°C , whereby a decrease in the optical rotation of $(0.5 \pm 0.3)\%$ was recorded within 2 h. This value is in accordance with the calculated decrease of optical rotation of 0.1% at this temperature within 2 h.

DNMR spectroscopy had given for the enantiomerization of *rac*-**4** a barrier of $\Delta G_{\text{enant}}^\ddagger = (17.8 \pm 0.3)\text{kcal mol}^{-1}$ at 333K . On the basis of the relationship $k_{\text{rac}} = 2k_{\text{enant}}$, the Eyring equation furnished for the enantiomerization of *rac*-**4** the thermodynamic parameters $\Delta H_{\text{rac}}^\ddagger = (16.7 \pm 0.3)\text{kcal mol}^{-1}$, $\Delta S_{\text{rac}}^\ddagger = (-3.3 \pm 1.1)\text{cal mol}^{-1}\text{K}^{-1}$, and a calculated barrier $\Delta G_{\text{rac}}^\ddagger = (17.8 \pm 0.3)\text{kcal mol}^{-1}$ at 333K . Thus, both methods, polarimetry and DNMR spectroscopy, gave the same results.

Determination of the racemization barrier of a nonracemic lithium (*S*)-trifluoromethylsulfonyl carbanion salt by time-dependent deuteration:

The racemization barrier of salt (*P*)-**5** was determined by time-dependent deuteration.^[4] This included the successive deprotonation of the enantiomerically pure triflone (*S*)-**13** and time-dependent deuteration of salt (*P*)-**5** with formation of triflone (*S*)-[**D**]**13** (Scheme 13). Tri-



Scheme 13. Synthesis and deuteration of salt (*P*)-**5**.

fione (*S*)-**13** was treated with *n*BuLi in THF at -78°C and, after a given time had elapsed, salt (*P*)-**5** was deuterated at -78°C with $\text{CF}_3\text{CO}_2\text{D}$. This gave the triflone (*S*)-[**D**]**13** with a D content of $\geq 98\%$, the *ee* value of which was determined by GC on a chiral stationary phase. From these experiments it followed that deprotonation of the *S*-configured triflone (*S*)-**13** with *n*BuLi gave with high selectivity the *P*-configured salt (*P*)-**5**, the deuteration of which also proceeded with high selectivity and yielded triflone (*S*)-[**D**]**13**. The isolation of triflone (*S*)-[**D**]**13** of 92% *ee* means that both the deprotonation of (*S*)-**13** and deuteration of (*P*)-**5** had, for example, occurred with calculated selectivities of 96% *ee*.

The *ee* value of the deuterated triflone (*S*)-[**D**]**13** is a function of the 1) selectivities of the deprotonation of triflone (*S*)-**13** and deuteration of salt (*P*)-**5** and 2) the extent of the racemization of the salt. On the basis of these considerations, the activation free energy of racemization of (*P*)-**5** was determined. A series of deprotonation–deuteration experiments was run in which all experimental parameters, in-

cluding those of deprotonation and deuteration, were kept constant except the time that elapsed after the addition of $n\text{BuLi}$ to triflone (S)-**13** and the beginning of the addition of $\text{CF}_3\text{CO}_2\text{D}$ to salt (P)-**5**, the racemization time t_{rac} (Table 4).

Table 4. Enantiomeric excess (ee) values of triflone (S)-[D]**13** in relation to the racemization time t_{rac} of salt (P)-**5** at 223 K.

t_{rac} [min]	10	30	45	60	120
ee [%]	83	82	79	76	71

Under these conditions, the enantioselectivities of deprotonation and deuteration were constant and the decrease in the ee value of (S)-[D]**13** only depended on t_{rac} . On the basis of first-order kinetics for the racemization of (P)-**5**, the ee value of (S)-[D]**13** can be described by Equations (3) and (4).^[4]

$$ee_{\text{D-sulfone}}(t_{\text{rac}}) = ee_0 \times e^{-k_{\text{rac}} \cdot t_{\text{rac}}} \quad (3)$$

$$\ln ee_{\text{D-sulfone}}(t_{\text{rac}}) = \ln ee_0 - k_{\text{rac}} t_{\text{rac}} \quad (4)$$

However, it is not possible to give the exact time for the completion of the deprotonation of triflone (S)-**13** and deuteration of (P)-**5** in these experiments. Deuteration experiments had shown that the deprotonation of triflone (S)-**13** with $n\text{BuLi}$ in THF at -78°C was complete after 2 min. Deuteration of salt (P)-**5** is a fast process and the termination of the racemization of the salt is practically determined by the time required for the addition of the acid. Thus, $t_{0\text{rac}}$ was set to 10 min, which included 5 min for the addition of $n\text{BuLi}$ and $\text{CF}_3\text{CO}_2\text{D}$ and 5 min for the completion of the deprotonation. In later experiments the time for the addition of the base and the deuteration reagent was kept constant and the time between the additions of both was increased. This led to Equations (5) and (6) for the determination of k_{rac} . The rate constant $k_{\text{rac}} = 2.48 \times 10^{-5} \text{ s}^{-1}$ was determined from the slope of a linear plot of $\ln ee_{\text{D-sulfone}}$ versus t_{rac} (Figure 9) and the activation free energy $\Delta G_{\text{rac}}^\ddagger = (17.6 \pm 0.2) \text{ kcal mol}^{-1}$ at 223 K was calculated with the aid of the Eyring equation.

$$ee_{\text{D-sulfone}}(t_{\text{rac}}) = ee(t_{0\text{rac}}) \times e^{-k_{\text{rac}}(t_{\text{rac}} - t_{0\text{rac}})} \quad (5)$$

$$\ln ee_{\text{D-sulfone}}(t_{\text{rac}} - t_{0\text{rac}}) = \text{const} - k_{\text{rac}}(t_{\text{rac}} - t_{0\text{rac}}) \quad (6)$$

In summary, the thermodynamic parameters for the enan-

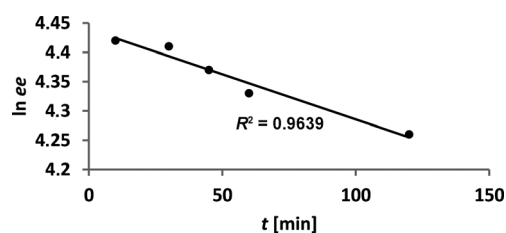


Figure 9. Dependence of $\ln ee$ of triflone (S)-**13** on the racemization time of salt (P)-**5** in THF at -50°C .

tiomerization of the (S)-trifluoromethylsulfonyl carbanion salts rac -**3a** and rac -**3b** and the racemization of (P)-**4** show that both are mainly enthalpic processes with small activation entropy, as is to be expected for processes in which C_α -S bond rotation is rate-determining. Particularly revealing are the very similar activation parameters obtained for the lithium salt rac -**3a**, tetrabutylammonium salt rac -**3b**, and potassium salt rac -**3c**. The lithium salt rac -**3a** and the tetrabutylammonium salt rac -**3b** exist in THF solution as monomeric CIPs (see below); they differ strongly in the nature of their ion pairing, whereas the potassium salt rac -**3c** forms free solvated ions in DMSO. Therefore, it follows that none of the following four processes can be the rate-determining steps of the enantiomerization/racemization: 1) the cleavage of the C_α -Li bond of a possible C_α -Li CIP, 2) the dissociation of the dimeric to the monomeric salts, 3) the conversion of monomeric CIPs that have two O-Li bonds to those with only one O-Li bond, or 4) the interconversion of diastereomeric CIPs with only one O-Li bond (see below). This is in accordance with the thermodynamic parameters recorded for the enantiomerization/racemization of the corresponding lithium (S)-*tert*-butylsulfonyl carbanion salts rac -**1**, rac -**4**, rac -**6**, and rac -**8**, respectively, is not possible because of the different temperatures. However, in consideration of the small activation entropy of (M)-**4**, the large differences in the activation energies indicate that there is a strong steric contribution of the substituents at the C_α atom to the enantiomerization barrier.

The increase of the configurational stability of the (S)-trifluoromethylsulfonyl and (S)-*tert*-butylsulfonyl carbanion salts (M)-**1a** and (M)-**4**, respectively, in THF upon addition of DMPU is most likely due to the formation of the corresponding CIPs (M)-**1a**·(THF)_{*n*}(DMPU)_{*o*}, (M)-**4**·(THF)_{*n*}(DMPU)_{*o*}, (M)-**1a**·(THF)_{*n*}(DMPU)_{*o*}, and (M)-**4**·(THF)_{*n*}(DMPU)_{*o*}, which have DMPU molecules coordinated to the Li atom (see below). This result points to a significant steric contribution of the bulky monodentate ligand DMPU at the Li atom to the rotational barrier of the O-Li CIP. The (S)-trifluoromethylsulfonyl carbanion salts have a significantly higher barrier towards C_α -S bond rotation and thus higher configurational stability than the corresponding α -(S)-butylsulfonyl (Tables 5 and 6) and α -(S)-phenylsulfonyl carbanion

Table 5. Thermodynamic parameters of the racemization of the (S)-*tert*-butylsulfonyl carbanion salts (P)-**1a** and (P)-**1a**/4DMPU and the (S)-trifluoromethylsulfonyl carbanion salt (M)-**4** in THF.

Parameter	(P)- 1a	(P)- 1a / DMPU ^[a]	(M)- 4	(M)- 4 / DMPU ^[a]
$\Delta G_{\text{rac}}^\ddagger$ [kcal mol ⁻¹]	12.9 ± 0.1 ^[b]	13.1 ± 0.3 ^[c]	17.2 ± 0.1 ^[d]	17.7 ± 0.1 ^[e]
$\Delta H_{\text{rac}}^\ddagger$ [kcal mol ⁻¹]	–	13.2 ± 0.3	16.7 ± 0.3	–
$\Delta S_{\text{rac}}^\ddagger$ [cal mol ⁻¹ K ⁻¹]	–	0.6 ± 1.2	–1.9 ± 1.1	–

[a] 4 equiv of DMPU. [b] At 187 K. [c] At 169 K. [d] At 239 K. [e] At 239 K.

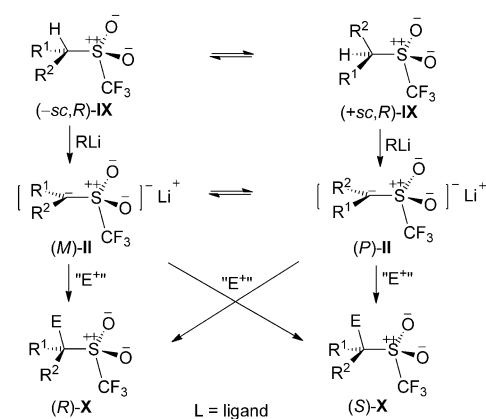
Table 6. Thermodynamic parameters of the enantiomerization of the benzylic lithium α -sulfonyl carbanion salt *rac*-**3a** and benzylic tetrabutylammonium α -sulfonyl carbanion salt *rac*-**3b** in THF.

Parameter	<i>rac</i> - 3a	<i>rac</i> - 3b
$\Delta G_{\text{enant}}^{\ddagger}$ [kcal mol ⁻¹]	15.9 ± 0.1 ^[a]	15.7 ± 0.2 ^[a]
$\Delta H_{\text{enant}}^{\ddagger}$ [kcal mol ⁻¹]	14.3 ± 0.5	14.6 ± 0.4
$\Delta S_{\text{enant}}^{\ddagger}$ [cal mol ⁻¹ K ⁻¹]	-5.2 ± 1	-3.9 ± 1

[a] At 298 K.

salts.^[3,4] Generally, the C_α-S rotational barrier is determined by steric and electronic effects. The steric effects primarily depend on the size and nature of the substituents at the C_α and S atoms. X-ray crystal structure analysis had shown a shorter C_α-S bond (2%) and longer S-C_{sp³} bond (1%) of the (*S*)-trifluoromethylsulfonyl carbanion salt (*M/P*)-**3a**·4THF than the corresponding α -(*S*)-*tert*-butylsulfonyl carbanion salt (see below). The shorter C_α-S bond could result in a higher C_α-S rotational barrier of the former salt. However, this effect might be outweighed by the longer S-R_F bond and the smaller steric effect exerted by the trifluoromethyl group as revealed by the Taft parameters (*E*_s(*t*Bu) = -2.78, *E*_s(CF₃) = -2.4),^[39a] rotational barriers of biphenyls,^[39b,c] and other data.^[39d] The calculations of the (*S*)-methylsulfonyl carbanion **III** and the (*S*)-trifluoromethylsulfonyl carbanion **IV** had shown the higher barrier of the latter to be due to the stronger n_C→σ*_{S-CF₃} interaction.^[6] Thus, the stronger n_C→σ*_{S-CF₃} interactions of salts **II** is an important contributing factor to their higher configurational stability (see below). The lower rotational barriers of the benzylic salts seem to be mainly due to the additional stabilization of the negative charge of the transition state by benzylic conjugation. From an inspection of the ground-state C_α-Ph conformation of the benzylic α -sulfonyl carbanions of salts *rac*-**3a-d** (see below) one would, at a first glance, expect a significant steric hinderance of the C_α-S bond rotation. However, this seems not to be the case. An ab initio study of the enantiomerization of [PhC(Me)SO₂*t*Bu]⁻ shows that C_α-S bond rotation is accompanied by a simultaneous partial rotation around the C_α-Ph and S-*t*Bu bonds to minimize steric interactions between the phenyl ring and the *t*Bu group.^[3]

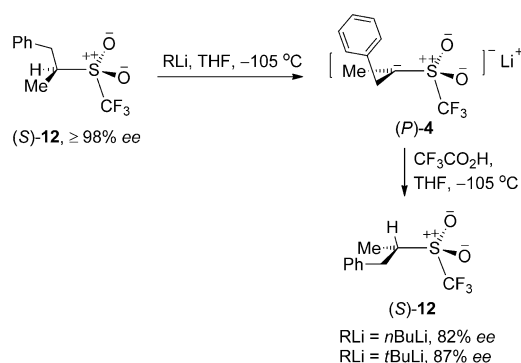
Enantioselective synthesis and electrophilic capture of lithium α -(*S*)-trifluoromethylsulfonyl carbanion salts: The determination of the racemization kinetics of salts (*M*)-**4** and (*P*)-**5**, both of which carry two alkyl groups at the anionic C atoms, revealed a relatively high configurational stability at -78 °C. The deprotonation of the enantiomerically pure triflones (*R*)-**12** and (*S*)-**13** with *n*BuLi occurred with high enantioselectivities, and the deuteration of salt (*P*)-**5** with CF₃CO₂D also proceeded with high enantioselectivities. On the basis of these results, further studies on the deprotonation of triflones (*R*)-**12** and (*S*)-**13** and reactions of salts (*M*)-**4** and (*P*)-**5** with C-based electrophiles were performed. In principle, the reaction of a given enantiomerically pure triflone, (*R*)-**IX**, with RLi can give both enantiomers of the



Scheme 14. Modes of deprotonation of chiral triflones and electrophilic capture of the corresponding chiral lithium α -(*S*)-trifluoromethylsulfonyl carbanion salts (priority: S > R¹ > R² > E).

α -trifluoromethylsulfonyl carbanion, (*M*)-**II** and (*P*)-**II**, depending on its conformation, (*-sc,R*)-**IX** and (*+sc,R*)-**IX**, in the transition state of deprotonation (Scheme 14). The reaction of the salts (*M*)-**II** and (*P*)-**II** with electrophiles can also give rise to the formation of both enantiomers of the substituted triflone, (*R*)-**X** and (*S*)-**X**, depending on the selectivity of the attack of the electrophile at the C_α atom of the carbanion. It is to be expected, however, that (*M*)-**II** and (*P*)-**II** will react at the C_α atom with electrophiles with high selectivities *anti* to the trifluoromethyl group.^[4]

The treatment of triflone (*S*)-**12** (≥ 98% *ee*) in THF at -105 °C with *n*BuLi in *n*-hexane and protonation of salt (*P*)-**4** with CF₃CO₂H at -105 °C gave triflone (*S*)-**12** of 82% *ee* in 97% yield (Scheme 15). The use of *t*BuLi in THF

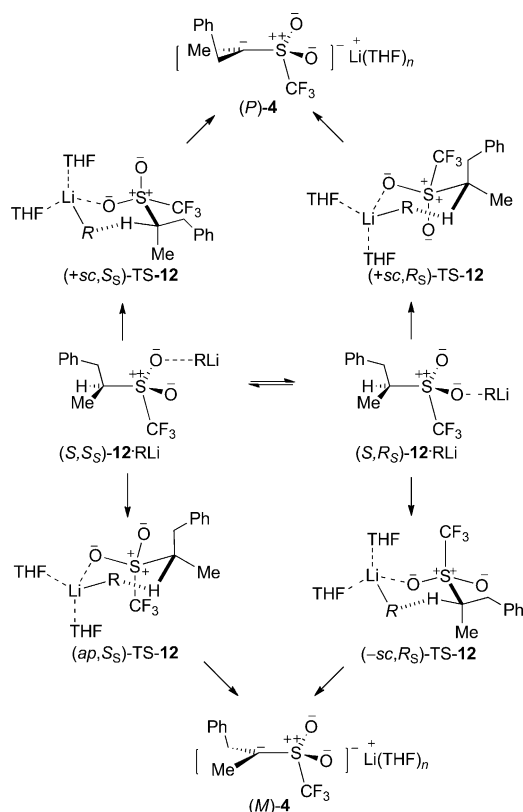


Scheme 15. Synthesis and protonation of salt (*P*)-**4**.

under otherwise identical conditions gave triflone (*S*)-**12** of 87% *ee* in 62% yield. The complete deprotonation of triflone (*S*)-**12** under these conditions was ensured in control quenching experiments with CF₃CO₂D, which were run under the same conditions and gave triflone (*S*)-[D]**12** of ≥ 97% D.

We had previously rationalized the enantioselectivity of the deprotonation of chiral (*S*)-*tert*-butyl sulfones with lithiumorganyls by assuming a prior complex formation be-

tween the sulfone and the base^[4,40] followed by an intramolecular proton transfer.^[14] Thus, it is proposed that triflone (*S*)-**12** also reacts with the lithiumorganyl by means of a prior reversible coordination to one of the O atoms with formation of the corresponding diastereomeric complexes (*S,S*)-**12**·RLi and (*S,R*)-**12**·RLi (Scheme 16). The complexa-



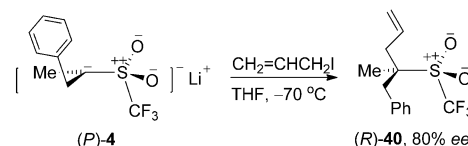
Scheme 16. Rationalization of the enantioselective deprotonation of triflone (*S*)-**12** (conformational descriptors refer to the C_{α} -S bond).

tion is followed by an intramolecular proton transfer by means of the cyclic six-membered transition states ($+sc,R_S$)-TS-**12** and ($+sc,S_S$)-TS-**12**, thus leading to the *P*-configured salt (*P*)-**4**, whereas proton transfer through transition states ($-sc,S_S$)-TS-**12** and (ap,R_S)-TS-**12** gives the corresponding *M*-configured salt (*M*)-**4**.

It is assumed that the factors that stabilize the lithium salt **4** are, at least to some extent, also effective in the stabilization of the transition states of deprotonation. Transition states ($-sc,R_S$)-TS-**12** and (ap,S_S)-TS-**12**, which lead to the *M*-configured salt, have a C_{α} -S conformation in which the bulky CF_3 group is in the pseudoaxial position. These transition states should be stabilized by $n_C \rightarrow \sigma^*_{S-O}$ and electrostatic interactions and destabilized by steric interactions. In contrast, transition states ($+sc,S_S$)-TS-**12** and ($+sc,R_S$)-TS-**12**, which lead to the *P*-configured salt, carry the CF_3 group in the pseudoequatorial position and are stabilized by $n_C \rightarrow \sigma^*_{S-CF_3}$ and electrostatic interactions. According to ab initio calculation of α -sulfonyl carbanions, the $n_C \rightarrow \sigma^*_{S-CF_3}$ interaction should be more stabilizing than the $n_C \rightarrow \sigma^*_{S-O}$ interac-

tion.^[3,41] Thus, because of electronic and steric reasons, transition states ($+sc,S_S$)-TS-**12** and ($+sc,R_S$)-TS-**12** should be preferred. In addition, on the way from transition state ($-sc,R_S$)-TS-**12** to salt (*M*)-**4**, the methyl group will have to move past the O atom through C_{α} -S bond rotation and rehybridization of the C_{α} atom. And on the way from transition state (ap,R_S)-TS-**12** to (*M*)-**4**, the benzyl group has to move past the O atom and the methyl group past the CF_3 group by means of C_{α} -S bond rotation and rehybridization of the C_{α} atom. In contrast, no such energetically costly movement of groups past atoms or groups is required on the way from transition states ($+sc,S_S$)-TS-**12** and ($+sc,R_S$)-TS-**12** to (*P*)-**4**. Because of the shielding of the anionic C atom of salt **4**, which is expected to be slightly pyramidalized (see below) by the trifluoromethyl group, deuteration of salt (*P*)-**4** with CF_3CO_2D gave triflone (*S*)-[D]**12** with high enantioselectivity.

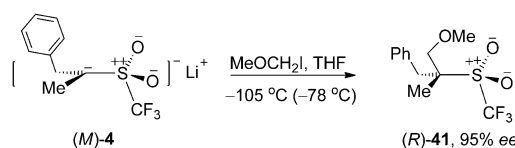
Next, the reactions of salts (*M*)-**4** and (*P*)-**4** with C-based electrophiles were studied. The treatment of salt (*P*)-**4** with allyl iodide in THF at $-70^\circ C$ for 1 d gave triflone (*R*)-**40** of 80% *ee* in 80% yield (Scheme 17). The *ee* value of (*R*)-**40**



Scheme 17. Allylation of salt (*P*)-**4**.

was initially determined by 1H NMR spectroscopy in the presence of AgFOD (FOD = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedioate) and [Pr(tfc)₃] (tfc = tris(3-trifluoromethylhydroxymethylene)-D-camphorate),^[42] and then by GC on a chiral stationary phase. Formation of (*R*)-**40** was not observed upon treatment of (*P*)-**4** with allyl iodide at $-100^\circ C$ for several hours.

Deprotonation of triflone (*R*)-**12** with *t*BuLi in THF at -105 or $-78^\circ C$ afforded salt (*M*)-**4**, the treatment of which with methoxymethyl iodide at -105 or $-78^\circ C$ gave triflone (*R*)-**41** of 95% *ee* in 78% yield (Scheme 18). The absolute



Scheme 18. Methoxymethylation of salt (*M*)-**4**.

configuration of triflone (*R*)-**41** was determined by X-ray crystal structure analysis (Figure 10).^[43] The reaction of (*M*)-**4** with methoxymethyl iodide was much faster than that of (*P*)-**4** with allyl iodide. Even at $-100^\circ C$, the alkylation was complete within 1 h.

With the methoxy-substituted triflone (*S*)-**41** in hand, we were interested to see whether a displacement of the triflyl group by an alkyl group would be possible under formation

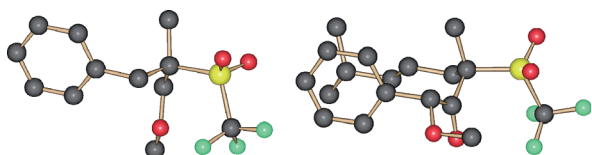
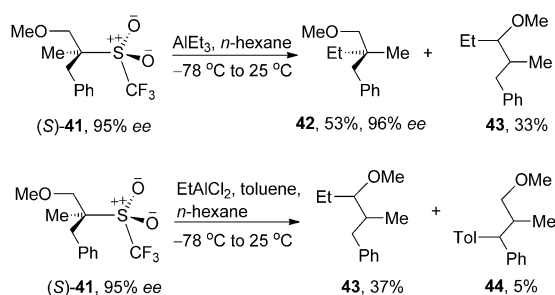


Figure 10. View of the crystal structures of triflones (*R*)-**41** (C_{α} -S 1.819(4), S-CF₃ 1.844(4) Å; left) and (*R,S*)-**52** (C_{α} -S 1.815(5), S-CF₃ 1.852(8) Å; right). Color code: C, black; S, yellow; O, red; F, green.

of a derivative with a sterogenic all-carbon quaternary C atom.^[44] The triflyl group is an excellent nucleofuge,^[45] and the alkylation of (*S*)-**41** with organometallics might be facilitated by their possible prior coordination to the methoxy group. In any event, the treatment of triflone (*S*)-**41** of 95% *ee* with AlEt₃ (4 equiv) in *n*-hexane gave the alkane **42** in 53% yield (Scheme 19). Remarkably, GC analysis of **42**

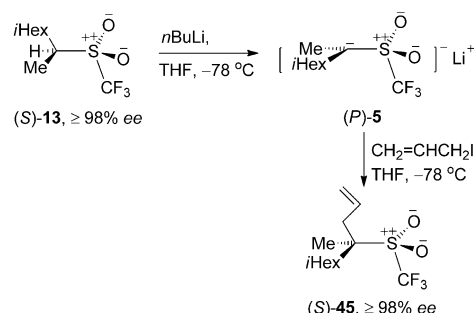


Scheme 19. Stereoselective alkylation of triflone (*S*)-**41** with AlEt₃.

on a chiral stationary phase showed the alkane to have an *ee* value of 96%. The absolute configuration of **42** was not determined, and in Scheme 21 the alkane is arbitrarily assigned the *R* configuration. The transformation of triflone (*S*)-**41** to alkane **42** is the first example of a highly stereoselective alkylation of a chiral nonallylic sulfone that has only one sterogenic center.^[46] In addition to **42**, alkane **43** was isolated in 33% yield as a 1:1 mixture of diastereomers, which were separated by HPLC. Interestingly, the treatment of triflone (*S*)-**41** with EtAlCl₂ in toluene/*n*-hexane did not afford **42** but gave the alkanes **43** in 37% yield and **44** in 5% yield, both as 1:1 and 2.5:1 mixtures of diastereomers, respectively. Presumably, **43** and **44** are derived from the triflone through ionization with the aluminum reagents and formation of the corresponding carbocation, which suffered competing hydrogen shifts under formation of the corresponding methoxy- and phenyl-stabilized carbocations. Whereas the reaction of the methoxy-stabilized carbocation with the aluminum reagents afforded **43**, trapping of the benzylic carbocation by toluene gave **44**.

To obtain a more complete picture of the synthesis of chiral lithium α -(*S*)-trifluoromethylsulfonyl carbanion salts and their reactivity towards C-based electrophiles, the reactions of the dialkyl-substituted salt (*P*)-**5** with alkylating and acylating reagents were studied. The deprotonation of triflone (*S*)-**13** with *n*BuLi and deuteration of salt (*P*)-**5** had

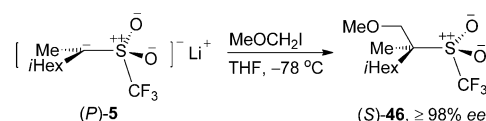
revealed high enantioselectivities for both reactions. Thus, salt (*P*)-**5** was generated from triflone (*S*)-**13** as described above and treated with allyl iodide at -78 °C, which afforded triflone (*S*)-**45** of $\geq 98\%$ *ee* (GC) in 59% yield (Scheme 20). According to NMR spectroscopy, the chemical



Scheme 20. Synthesis and allylation of salt (*P*)-**5**.

yield of (*S*)-**45** was approximately 90%. Methoxymethylation of salt (*P*)-**5** proceeded with equally high enantioselectivity. Thus, treatment of (*P*)-**5** with methoxymethyl iodide in THF at -78 °C gave triflone (*S*)-**46** of $\geq 98\%$ *ee* in 78% yield (Scheme 21).

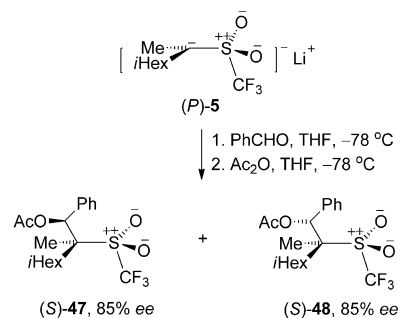
Next, the reactions of salt (*P*)-**5** with aldehydes and acid



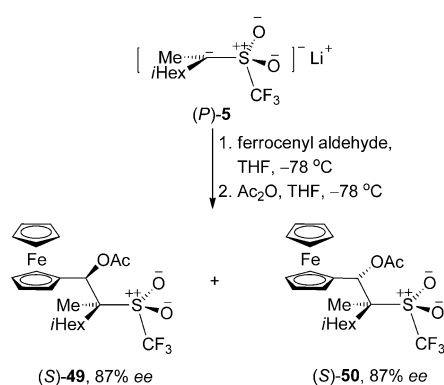
Scheme 21. Methoxymethylation of salt (*P*)-**5**.

chlorides were investigated. The treatment of salt (*P*)-**5** with benzaldehyde and the trapping of the intermediate lithium alkoxides with acetic anhydride at low temperatures afforded a mixture of the acetates (*S*)-**47** and (*S*)-**48** in a ratio of 1.7:1 in 67% yield. Both isomeric acetates had an *ee* value of 85% as revealed by ¹H NMR spectroscopy in the presence of 1-(anthracen-9-yl)-2,2,2-trifluoroethanol (Pirkle alcohol)^[47] (Scheme 22).

A similar reaction of salt (*P*)-**5** with ferrocenyl aldehyde and trapping of the intermediate lithium alkoxides with acetic anhydride furnished a mixture of the acetates (*S*)-**49**

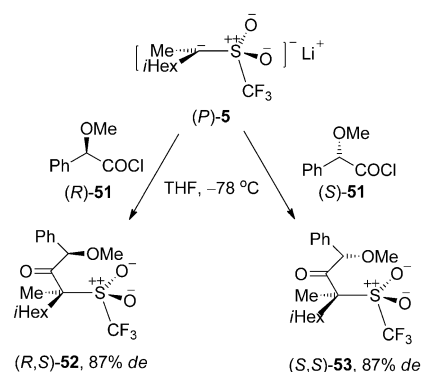


Scheme 22. Hydroxyalkylation of salt (*P*)-**5** with benzaldehyde.



Scheme 23. Hydroxyalkylation of salt (P)-5 with ferrocenyl aldehyde.

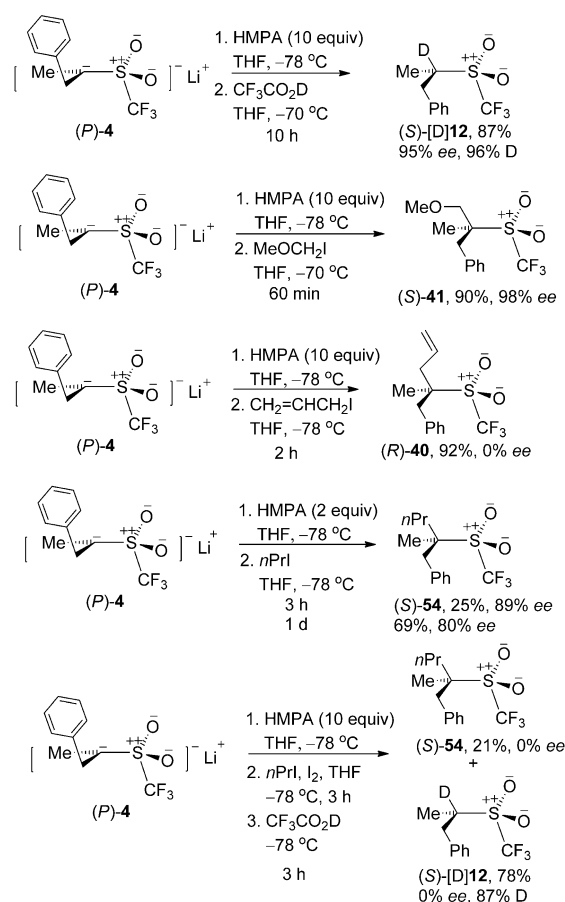
of 87% *ee* and (S)-50 of 87% *ee* in a ratio of 3:2 in 65% yield (Scheme 23). The *ee* values of both acetates were determined by ^1H NMR spectroscopy in the presence of Pirkle alcohol. The reactions of salt (P)-5 with the acid chlorides (R)-51 and (S)-51 were studied to obtain information about the reactivity of the salt towards acylation reagents and to hopefully obtain crystalline derivatives for a determination of their absolute configuration by means of X-ray crystal structure analysis. The treatment of salt (P)-5 with the acid chloride (R)-51 ($\geq 98\%$ *ee*) in THF at low temperatures furnished the crystalline ketone (R,S)-52 of 87% diastereomeric excess (*de*) (^1H NMR spectroscopy, Pirkle alcohol) in 67% yield (Scheme 24). A similar reaction of (P)-5 with



Scheme 24. Acylation of salt (P)-5 with chiral acid chlorides.

(S)-51 ($\geq 98\%$ *ee*) gave the oily ketone (S,S)-53 of 87% *de* (^1H NMR, Pirkle alcohol) in 72% yield. Determination of the relative configuration of ketone (R,S)-52 was made by X-ray crystal structure analysis (see Figure 10).^[43] Because of the *R* configuration of (R)-51, the C_α atom of (R,S)-52 has the *S* configuration. On the basis of the absolute configurations of (R)-41 and (R,S)-52 those of the other triflones derived from the salts (P)-4 and (P)-5 were assigned as depicted in Schemes 17, and 20–23. It follows from these assignments that the two-step formation of the tertiary triflones from the secondary triflones proceeds under retention of configuration.

Reactivity in the presence of HMPA: Previous studies of lithium α -sulfonyl carbanion salts had shown that the addition of increasing amounts of HMPA leads to a successive replacement of the THF molecules coordinated to the Li atom of the CIP by HMPA molecules and the final formation of the corresponding solvent-separated ion pairs (SIPs).^[3,4,48] Therefore, the influence of HMPA upon the selectivity of the reactions of salt (P)-4 with electrophiles and its reactivity was probed. Triflone (S)-12 in THF was treated at $-78\text{ }^{\circ}\text{C}$, a temperature at which racemization is negligible on the timescale of deprotonation and deuteration, with *t*BuLi in *n*-pentane. Then salt (P)-4 was successively treated with cold solutions of HMPA (10 equiv) in THF at $-78\text{ }^{\circ}\text{C}$ and $\text{CF}_3\text{CO}_2\text{D}$ in THF at $-70\text{ }^{\circ}\text{C}$ (Scheme 25). Triflone (S)-



Scheme 25. Reactions of salt (P)-4 with electrophiles in the presence of HMPA.

[D]12 of 95% *ee* and 96% D was isolated in 87% yield. Thus, as in the case of the corresponding (S)-*tert*-butyl sulfone and salt,^[4] the deuteration of salt (P)-4 in the presence of HMPA occurred with high enantioselectivity. The successive treatment of salt (P)-4 with cold ($-70\text{ }^{\circ}\text{C}$) solutions of HMPA (10 equiv) in THF and methoxymethyl iodide in THF at -78 and $-70\text{ }^{\circ}\text{C}$, respectively, furnished triflone (S)-41 of 98% *ee* in 90% yield. The *ee* value of (S)-41 was de-

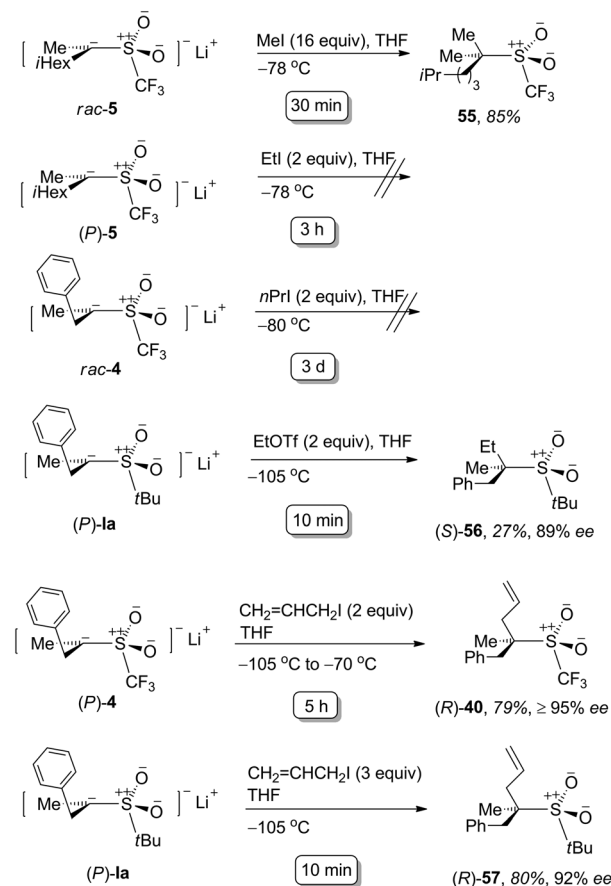
terminated by GC on a chiral stationary phase. The isolation of (*S*)-**41** of 98% *ee* translates into calculated selectivities of, for example, 99% *ee* for both deprotonation and alkylation. Salt (*P*)-**4** is expected to form in the presence of 10 equiv of predominantly HMPA-coordinated SIPs in addition to monomeric HMPA-coordinated Li–O CIPs.^[3,4,48] Because of the high overall selectivity of the methoxymethylation of (*P*)-**4**/10HMPA, one can safely assume that not only the CIPs but also the SIPs of (*P*)-**4** exhibit high enantioselectivities towards electrophiles.

The allylation of salt (*P*)-**4** with allyl iodide in THF at –70°C was rather slow and had given triflone (*R*)-**40** with an *ee* value of only 80% (see Scheme 17). It was therefore of interest to see whether an HMPA-coordinated SIP of (*P*)-**4** would show a higher reactivity than the corresponding THF-coordinated CIP. Treatment of salt (*P*)-**4** with HMPA (10 equiv) and allyl iodide resulted in a much shorter reaction time and gave triflone *rac*-**4** in 90% yield. Surprisingly, the triflone was essentially racemic, thus indicating that a racemization of the salt had occurred. Although the sample of allyl iodide that was used in the allylation was purified by passing through basic alumina, it still might have contained traces of iodine. Because of speculations that the combination of iodine and HMPA might have caused the racemization of salt (*P*)-**4** in the above experiment, a control experiment with *n*-propyl iodide, which could be completely freed of iodine, was performed. Whereas salt (*P*)-**4** did not react with *n*PrI at –78°C in THF for an extended period of time, successive treatment of the salt with HMPA (2 equiv) and purified *n*PrI furnished triflone (*S*)-**54** of 89% *ee* in 25% yield after a reaction time of 3 h. An extension of the reaction time to 1 d gave triflone (*S*)-**54** of 80% *ee* in 69% yield. Next, salt (*P*)-**4** was successively treated with HMPA (10 equiv) and a mixture of *n*PrI and of iodine (0.1 equiv) in THF at –78°C. Then the mixture was quenched at low temperatures with CF₃CO₂D. This sequence of events led to the isolation of the racemic triflone *rac*-**54** in 21% yield and the racemic starting triflone *rac*-[D]**12** in 78% yield with a D content of 87%. Similar observations were made in the case of salt (*P*)-**5**. Whereas (*P*)-**5** had afforded triflone (*S*)-**45** with ≥98% *ee* upon treatment with purified allyl iodide in THF at –78°C, a similar reaction in the presence of HMPA (10 equiv) gave the triflone in 35% yield with only 28% *ee*. Thus, in the presence of iodine and HMPA, and perhaps iodide salts (*P*)-**4** and (*P*)-**5** had partially or completely racemized. Further investigations aimed at uncovering the mechanism of the racemization that was not observed if only HMPA was present were not conducted.

Reactivity of lithium (*S*)-trifluoromethyl- and (*S*)-*tert*-butylsulfonyl carbanion salts: Comparative reactivity studies of α-trifluoromethyl and α-phenylsulfonyl carbanions in DMSO, DMSO/water, and in MeOH, in which the carbanions exist as solvated counterion-free species, revealed a much lower nucleophilicity of the fluorinated carbanions.^[10] Information on the reactivity of their lithium salts in THF, which would be of particular synthetic relevance, were, how-

ever, not available. Therefore, we conducted a qualitative study of the reactivity of the lithium (*S*)-trifluoromethylsulfonyl carbanion salts (*P*)-**4**, *rac*-**4**, *rac*-**5**, and (*P*)-**5**, and the (*S*)-*tert*-butylsulfonyl carbanion salt (*P*)-**1a** in THF, a solvent in which the salts exist as O–Li CIPs (see below).

The reaction of the (*S*)-trifluoromethylsulfonyl carbanion salt *rac*-**5** with MeI (16 equiv) at –78°C was fast, and quenching of the mixture after 30 min gave triflone **55** in 85% yield (Scheme 26). Under similar conditions, no alkyla-



Scheme 26. Reactivity of lithium α-(*S*)-trifluoromethyl- and α-(*S*)-*tert*-butylsulfonyl carbanion salts towards C-based electrophiles.

tion was observed upon the treatment of salt (*P*)-**5** with EtI (2 equiv) for 3 h at –78°C. Similarly, the treatment of the (*S*)-trifluoromethylsulfonyl carbanion salt *rac*-**4** with *n*PrI (2 equiv) at –80°C for 3 d led to no alkylation of the salt. In contrast, treatment of the (*S*)-*tert*-butylsulfonyl carbanion salt (*P*)-**1a** with EtOTf (Tf = SO₂CF₃) (2 equiv) at –105°C for 10 min gave sulfone (*S*)-**56** in 27% yield. Although different electrophiles were applied in the experiments with (*P*)-**5** and (*P*)-**1a**, the results obtained pointed to a significantly lower reactivity of the (*S*)-trifluoromethylsulfonyl carbanion salt. To allow for a better comparison, the reactivity of salts (*P*)-**4** and (*P*)-**1a** towards allyl iodide was investigated. An allylation of the (*S*)-trifluoromethylsulfonyl carbanion salt (*P*)-**4** was not noticed when the salt and allyl iodide

(2 equiv) were kept at -90°C for 5 h. In a second experiment, salt (*P*)-**4** was treated with allyl iodide (2 equiv) at -70°C for 5 h, which gave triflone (*R*)-**40** in 79% yield. In strong contrast, the treatment of the (*S*)-*tert*-butylsulfonyl carbanion salt (*P*)-**1a** with allyl iodide (3 equiv) at -105°C for only 10 min gave sulfone (*R*)-**57** in 80% yield.^[4] These results show that the CIPs of the lithium α -(*S*)-trifluoromethylsulfonyl carbanion salts have a significantly lower reactivity towards C-based electrophiles than the corresponding CIPs of the lithium (*S*)-*tert*-butylsulfonyl carbanion salts.

Structure of α -(*S*)-trifluoromethylsulfonyl carbanion salts in the crystal phase: Ab initio calculations of counterion-free α -(*S*)-trifluoromethyl and α -(*S*)-methylsulfonyl carbanions^[6] and the kinetic experiments with salts **I**^[3] and **II** revealed significant differences in their racemization dynamics. Therefore, it was of interest to see whether also significant structural differences exist between the α -(*S*)-trifluoromethyl- and α -(*S*)-*tert*-butylsulfonyl carbanion salts. The dimeric lithium (*S*)-trifluoromethylsulfonyl carbanion salts (*M/P*)-**3a**·4THF^[5b] and (*M/P*)-**3a**·2TMEDA (TMEDA = tetramethylethylenediamine; Figure 11)^[5a] have in the crystal phase similar centrosymmetric O–Li CIP structures to the corresponding dimeric (*S*)-*tert*-butylsulfonyl carbanion salt (*M/P*)-**1b**·4THF.^[3] Both salts contain the typical chiral carbanions, which are characterized by 1) a C_{α} –S conformation in which the lone pair orbital at the anionic C atom bisects the O–S–O angle, 2) an almost planar anionic C atom, 3) the absence of bonds between the C_{α} and Li atoms, and 4) the presence of O–Li bonds. The phenyl ring at the C_{α} atom adopts a C_{α} –Ph conformation, which allows for an interaction between the orbital at the C_{α} atom and the π system of the phenyl ring as judged by the dihedral angle S– C_{α} –C_i–C_o (Table 7). The deviations from the optimal dihedral angle for conjugation in the (*S*)-trifluoromethylsulfonyl carbanion salts (*M/P*)-**3a**·4THF and (*M/P*)-**3a**·2TMEDA are somewhat larger than in the (*S*)-*tert*-butylsulfonyl carbanion salt (*M/P*)-**1b**·4THF.^[3] A comparison of the crystal structures of the (*S*)-trifluoromethylsulfonyl carbanion salts (*M/P*)-**3a**·4THF and (*M/P*)-**3a**·2TMEDA with those of the dimeric (*S*)-*tert*-butylsulfonyl carbanion salt (*M/P*)-**1b**·4THF and the monomeric salt *rac*-**1b**·12c4 (12c4 = 12-crown-4), which is also an O–Li CIP,^[3] reveals a shorter C_{α} –S bond and a longer S–C bond of the fluorinated salts. It should be noted, however, that the C_{α} –S and S–C bonds of the parent triflone *rac*-**11**^[5a] are already shorter and longer, respectively, than those of the (*S*)-*tert*-butylsulfone *rac*-**58**.^[4] The shortening of the C_{α} –S bonds of the sulfones *rac*-**58** and *rac*-**11** upon deprotonation with formation of the corresponding salts (*M/P*)-**3a**·4THF and (*M/P*)-**1b**·4THF amounts to 9 and 10%, respectively. Thus, one of the major structural reorganizations that occurs upon deprotonation of sulfones *rac*-**11** and *rac*-**57** might be seen in the considerable shortening of the C_{α} –S bond. The C_{α} –S bond of the (*S*)-tri-

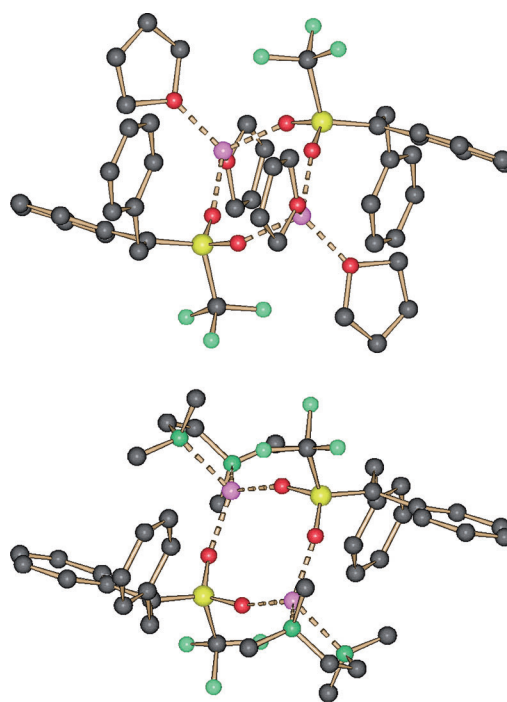
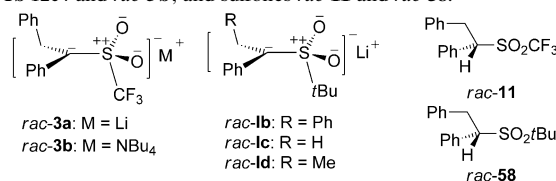


Figure 11. View of the crystal structures of the dimeric lithium salts (*M/P*)-**3a**·4THF (top)^[5b] and (*M/P*)-**3a**·2TMEDA (bottom).^[5a] Color code: C, black; S, yellow; O, red; N, blue; Li, pink; F, green.

Table 7. Selected bond lengths [Å], bond angles [°], and dihedral angles [°] of the dimeric salts (*M/P*)-**1b**·4THF, (*M/P*)-**3a**·4THF, and (*M/P*)-**3a**·2TMEDA; the monomeric salts *rac*-**1b**·12c4 and *rac*-**3b**; and sulfones *rac*-**11** and *rac*-**58**.



Salt/Sulfone	C_{α} –S	S–C	C_{α} –Ph	$\Sigma[<(C_{\alpha})]$	S– C_{α} –C _i –C _o
(<i>M/P</i>)- 3a ·4THF	1.620(3)	1.859(3)	1.467(3)	359.9	15.5
(<i>M/P</i>)- 3a ·2TMEDA	1.608(6)	1.856(6)	1.455(9)	359.9	15.5
<i>rac</i> - 3b	1.638(4)	1.838(2)	1.468(5)	359.5	8.5
<i>rac</i> - 11	1.807(3)	1.850(6)	1.518(4)	–	–
(<i>M/P</i>)- 1b ·4THF	1.659(2)	1.838(2)	1.451(3)	359.9	10.5
<i>rac</i> - 1b ·12c4	1.68(1)	1.841(8)	1.45(1)	359.7	–5.9
<i>rac</i> - 58	1.830(2)	1.822(2)	1.504(3)	–	–
Ic ·PMDTA	1.675(4)	1.829(4)	1.429(5)	360.0	6.2
(<i>M/P</i>)- 1d ·4THF	1.676(7)	1.821(8)	1.42(1)	359.9	–4.5

fluoromethylsulfonyl carbanion salt (*M/P*)-**3a**·4THF is 2% shorter and the S–C bond is 1% longer than the corresponding bonds of the (*S*)-*tert*-butylsulfonyl carbanion salts (*M/P*)-**1b**·4THF. It should be emphasized, however, that these differences in bond lengths are, as pointed out above, already manifested in the corresponding sulfones.

It is interesting to compare the structure of the lithium salt (*M/P*)-**3a**·4THF with that of the corresponding tetrabutylammonium salt *rac*-**3b** in the crystal phase (Figure 12).^[5b] The structure of *rac*-**3b** is characterized by an interaction

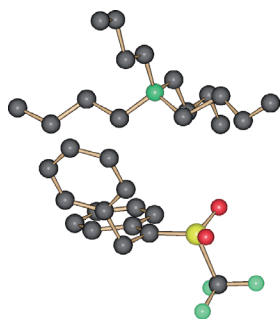


Figure 12. View of the crystal structure of the tetrabutylammonium salt *rac-3b*.^[5b] Color code: C, black; S, yellow; O, red; Li, pink; N, blue; F, green.

between the anion and cation through presumably weak C–H...O hydrogen bonds that involve the O atoms and the H atoms at the α position to the N atom of two cations. The tetrabutylammonium salt [PhC(H)SO₂Ph]NBu₄ exhibits similar hydrogen bonds in the crystal phase.^[49] Despite the very different interactions between the carbanions and cations in salts (*M/P*)-**3a**·4THF and *rac-3b*, the carbanions of both salts have very similar structures. In the lithium salt (*M/P*)-**3a**·4THF, the dihedral angle S–C _{α} –C₁–C₀ is larger than in the ammonium salt *rac-3b*. The larger dihedral angle of the lithium salt is most likely the result of a steric interaction between the phenyl ring and the THF molecules within the centrosymmetric dimer. Whereas the S–O bonds of *rac-3b* and (*M/P*)-**3a**·4THF are nearly identical in length, the C _{α} –S bond of the lithium salt (*M/P*)-**3a**·4THF is 0.018 Å shorter and the S–CF₃ bond is 0.021 Å longer than in the ammonium salt *rac-3b*.

Structure of α -(*S*)-trifluoromethylsulfonyl carbanion salts in solution

Aggregation and ion pairing: The salts *rac-3a–c*, *rac-4*, *rac-5*, and *rac-1a–d*^[3] were investigated by NMR spectroscopy to gain further information on the structural differences between α -(*S*)-trifluoromethyl- and α -(*S*)-*tert*-butylsulfonyl carbanion salts, the modes of their ion pairing, and the benzylic conjugation. The (*S*)-trifluoromethylsulfonyl carbanion salts *rac-3a–c*, which have different cations, were studied in [D₆]DMSO and [D₈]THF to determine the influence of the ion pairing upon the electronic structure of the carbanion. Whereas the potassium salt *rac-3c* should mainly form in [D₆]DMSO counterion-free solvated carbanions,^[7] the tetrabutylammonium salt *rac-3b* and the lithium salt *rac-3a* are expected to exist in [D₈]THF as CIPs. According to cryoscopy, the lithium salts *rac-3a* and *rac-5* predominantly form monomers at –108 °C in THF (Table 8). In contrast, the (*S*)-*tert*-butylsulfonyl carbanion salts *rac-1* form nearly 1:1 mixtures of monomers and dimers at –108 °C in THF.^[3] Likely structures of the monomeric CIPs of lithium α -sulfonyl carbanion salts are **A–C** (Figure 13). CIP **A** has two O–Li bonds, CIP **B** exhibits only one O–Li bond, and CIP **C** features both an O–Li and a C _{α} –Li bond. Whereas the Li atoms of CIPs **A** and **C** carry two ligand molecules, the Li atom of CIP **B** has three ligand molecules. In the crystal phase, a CIP of type **B** had been observed for *rac-1b*·12c4, *rac-1c*·PMDTA (PMDTA = pentamethyldiethylenetriamine), and *rac-1e*·PMDTA (Figure 14), the Li atoms of which are coordinated by the tetradentate ligand 12c4 and tridentate

Table 8. Aggregation of the (*S*)-trifluoromethylsulfonyl carbanion salts *rac-3a*, *rac-3b*, and *rac-5* at –108 °C in THF.

Entry	Salt	<i>c</i> [mmol kg ^{–1}]	<i>N</i> ± σ	M/D
1	<i>rac-3a</i>	85.06	1.06 ± 0.3	94:6
2	<i>rac-3a</i>	165.49	1.08 ± 0.3	92:8
3	<i>rac-3b</i>	48.5 ^[a]	≈ 1.12	–
4	<i>rac-5</i>	38.27	1.06 ± 0.3	96:4

[a] A small amount of the salt crystallized during the measurements.

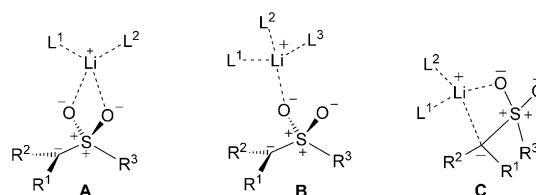


Figure 13. Likely structures of the monomeric CIPs **A–C** of lithium α -sulfonyl carbanion salts (diastereomers of **B** and **C** are omitted for clarity; L¹, L², L³ = THF, DMPU, HMPA).

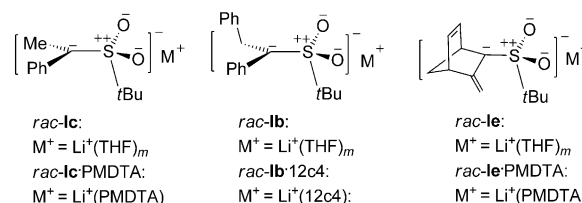


Figure 14. Lithium α -(*S*)-*tert*-butylsulfonyl salts containing different ligands.

ligand PMDTA, respectively.^[3,41a] NMR spectroscopy of *rac-1b–d* in THF at low temperatures, at which the salts form mixtures of monomers and dimers, revealed up to four rapidly interconverting species, the identification of which was not possible because of very similar chemical shifts.^[3,40a]

X-ray crystal structure analysis of dimethoxyethane-coordinated 2,2-diphenyl-1-(phenylsulfonyl)cyclopropyllithium revealed a dimer with two four-membered rings composed of the C _{α} , S, O, and Li atoms as in CIP **C**.^[50] However, this lithium α -sulfonyl carbanion salt seems to be a special case because of the strong pyramidalization of the C _{α} atom embedded in the three-membered ring. X-ray crystal structure analysis of the solvate-depleted polymeric salt {[MeC(H)SO₂Ph]Li·THF} _{∞} ^[51a] and the solvate-free salt {[Me-nOCH₂CH₂C(H)SO₂Ph]}₄Li (OMen = menthyl)^[51b] demonstrated the presence of O–Li and C _{α} –Li bonds, which are, however, not incorporated into a four-membered as in **C**. The tetrabutylammonium salt *rac-3b* predominantly forms a monomer in THF at low temperatures according to the cryoscopic experiments (see Table 8). The CIPs of *rac-3a* and *rac-3b* will differ significantly in regard to the nature of the

ion pairing. Whereas the CIPs of the lithium salt *rac*-**3a** all feature at least one strong bond between an O atom of the carbanion and the Li atom, which has a high positive charge density, the CIP of the tetrabutylammonium salt *rac*-**3b** most likely exhibits, as in the crystal phase (see above),^[5b] several weak C–H \cdots O bonds between the carbanion and the large tetrabutylammonium ion, which possesses a low positive charge density.

To gain further information on the ion pairing of *rac*-**3a**, the salt was submitted to homo- and heteronuclear nuclear Overhauser effect (NOE) experiments in $[D_8]THF$ in the presence of the bidentate ligand TMEDA. Solutions of the salt were prepared by using crystalline (*M/P*)-**3a**·TMEDA labeled with 6Li (95%). It is assumed that *rac*-**3a** also forms monomers in $[D_8]THF$ in the presence of TMEDA. 1D- $^6Li\{^1H\}$ NOE and $^1H,^6Li$ HOESY experiments^[52] at room temperature revealed strong effects between the Li atom and the Me and CH_2 groups of TMEDA, weak effects between the Li atom and the *o*-H atoms of both phenyl groups, and medium effects, which are different in magnitude, between the Li atom and the benzylic hydrogen atoms. The $^6Li\{^1H\}$ NOE and $^1H,^6Li$ HOESY experiments of *rac*-**3a**·TMEDA at $-70^\circ C$, in which C_α –S bond rotation is slow on the timescale of the NOE experiments, gave the same results. $^6Li\{^{19}F\}$ NOE experiments at room temperature showed a strong effect between the F atoms and the Li atom, whereas $^1H\{^{19}F\}$ NOE experiments gave strong effects between the F atoms and the *o*-H atoms of both phenyl groups, a medium effect between the F atoms and the Me groups, and weak effects between the F atoms and the CH_2 groups of the benzyl group and TMEDA. $^1H\{^1H\}$ NOE experiments at $-20^\circ C$ only showed, in addition to medium effects between the benzylic H atoms and the *o*-H atoms of both phenyl groups, weak effects between the Me groups and the *o*-H atoms of both phenyl rings. The NOE experiments clearly show that salt *rac*-**3a** exists in THF solution as CIP(s), the Li atom(s) of which is (or are) coordinated by TMEDA. Likely structures of the TMEDA-containing CIPs of *rac*-**3a** are depicted in Figure 15. Whereas CIP **3aA** has two O–Li bonds and carries one TMEDA molecule, the diastereomeric CIPs **3aB** exhibit one O–Li bond and also have a THF molecule in addition to a TMEDA molecule, and the diastereomeric CIPs **3aC** feature O–Li and C–Li bonds and contain one TMEDA molecule. On the basis of the crystal structure of the monomeric CIP *rac*-**1b**·12c4,^[3] the diastereomeric CIPs **3aB** are expected to have a C_α – C_β conformation as depicted. The NOE data would be more consistent with CIPs **3aA** and **3aB**. In particular, the $^1H\{^1H\}$ and $^6Li\{^1H\}$ NOE data make CIPs **3aC** with a C_α –Li bond and an sp^3 -hybridized C_α atom less likely as the major species. This is supported by the analysis of the charge distribution of salts *rac*-**3a**–**c** on the basis of their NMR spectroscopic data and ab initio calculations (see below). Although the NMR spectra of *rac*-**3a**/TMEDA at $-70^\circ C$ showed only a single species, the existence of a fast equilibrium, which involves **3aA** and/or **3aB** and to some extent also **3aC**, cannot be excluded.

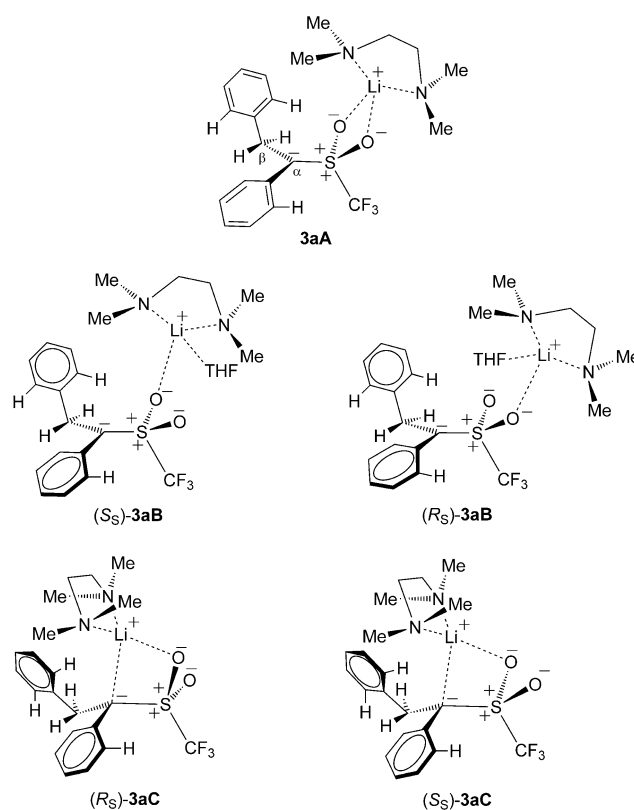


Figure 15. Likely structures of monomeric CIPs **A**–**C** of the lithium salt *rac*-**3a** in the presence of TMEDA in THF (the other *o*-H atoms of the phenyl rings are omitted because of clarity).

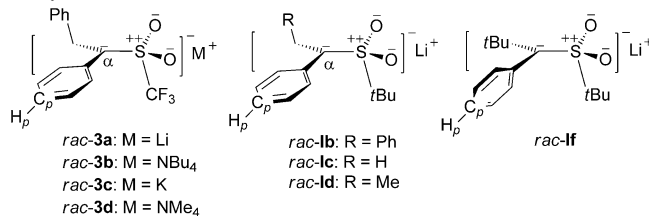
$^1H\{^1H\}$ NOE and $^6Li\{^1H\}$ NOE experiments on the (*S*)-*tert*-butylsulfonyl carbanion salts *rac*-**1b** and *rac*-**1e** in $[D_8]THF$ had given similar results to those of *rac*-**3a**/TMEDA.^[53a,b] However, interpretation of the NOEs of the α -(*S*)-*tert*-butylsulfonyl carbanion salts was complicated by the existence of monomers and dimers in nearly equal amounts, since they were in rapid equilibrium even at low temperatures.

Stabilization and charge distribution: The negative charge of salts *rac*-**3**, *rac*-**4**, and *rac*-**1** is stabilized by the sulfonyl groups. However, the stabilization of the (*S*)-*tert*-butylsulfonyl and (*S*)-trifluoromethylsulfonyl salts is expected to strongly differ in magnitude, given the large difference in acidity between, for example, $PhCH_2SO_2tBu$ and $PhCH_2SO_2CF_3$ ($\Delta pK_a = -10.3$; both with K^+ as counterion in DMSO).^[7] The negative charge of *rac*-**3**, *rac*-**4**, and *rac*-**1** should also be significantly stabilized by the phenyl group. For example, the acidity of both sulfones $MeSO_2tBu$ ($\Delta pK_a = -5.4$) and $MeSO_2CF_3$ ($\Delta pK_a = -4.4$) (with K^+ in DMSO) strongly increases upon substitution of an α -H atom by a phenyl group.^[7] Surprisingly, despite the large increase in acidity in going from $MeSO_2CF_3$ to $PhCH_2SO_2CF_3$, the benzylic conjugation in salt $[PhC(H)SO_2CF_3]NMe_4$ (DMSO) was characterized as not being of appreciable importance on the basis of its ^{13}C NMR spectroscopic data.^[9] It

was therefore of particular interest to see what the magnitude of the benzylic interaction in the (*S*)-trifluoromethylsulfonyl salts *rac*-**3a–c** and (*S*)-*tert*-butylsulfonyl carbanion salts *rac*-**1b–d** is and whether or not there is a difference in conjugation between both types of salts. The triflone PhCH₂SO₂CF₃ has a 1 pK unit lower acidity than the *tert*-butylsulfone PhCH₂SO₂*t*Bu, perhaps indicating that benzylic interaction in (*S*)-trifluoromethylsulfonyl carbanions is somewhat less than in (*S*)-*tert*-butylsulfonyl carbanions. Generally, appropriate NMR spectroscopic monitors for the electronic interaction in benzylic carbanions are the shift differences, $\Delta\delta H_p$ and $\Delta\delta C_p$ (*para* monitors), for the atoms in the *para* position of the phenyl group on going from the CH acid to the corresponding carbanion.^[54,55] The interaction of the negative charge with the phenyl group by means of conjugation and/or π polarization^[54–56] causes an increase in negative charge density at the *para* position and thus an upfield shift of the corresponding ¹H and ¹³C signals. An inspection of Table 9 shows a strong upfield shift of the signals

A and **B** of the salts will have C_α–Ph and C_α–S conformations and C_α coordination geometries in solution, which would be significantly different to those in the crystal phase. Of particular importance for the mode and magnitude of the benzylic interaction is the C_α–Ph conformation. An inspection of Tables 7 and 9 shows that deviations of the S–C_α–C_i–C_o dihedral angle up to approximately ±15° do not noticeably hinder the conjugative benzylic interaction in carbanions *rac*-**3a–c** and *rac*-**1c, d**.^[3] In contrast to the benzylic conjugation, the polarization of the π system by the negative charge is independent of the dihedral angle. This is demonstrated by a comparison of salts *rac*-**1b**–**12c4** and *rac*-**1f**, which have dihedral angles of –5.9° (see Table 7) and 77°,^[3] respectively, in the crystal phase. The $\Delta\delta H_p$ and $\Delta\delta C_p$ values of salt *rac*-**1f**, carrying a *tert*-butyl group at the C_α atom, are much smaller than those of salt *rac*-**1b** (Table 9, entries 9 and 13).^[3] Thus, the accumulation of negative charge at C_p of *rac*-**1f** through polarization of the π system is significantly smaller than at C_p of *rac*-**1b** through conjugation. The difference in $\Delta\delta H_p$ and $\Delta\delta C_p$ of both salts proves at the same time the existence of a significant benzylic conjugation in salts *rac*-**3a–c** and *rac*-**1b–d**.

Table 9. Selected NMR spectroscopic data of the benzylic (*S*)-trifluoromethylsulfonyl carbanion salts *rac*-**3a–d** and (*S*)-*tert*-butylsulfonyl carbanion salts *rac*-**1b–d** and *rac*-**1f**.^[a–d]



Entry	Salt	Solvent ^[e]	c ^[f]	$\Delta\delta H_p$ (δH_p)	$\Delta\delta C_p$ (δC_p)	$\Delta\delta C_\alpha$ (δC_α)
1	<i>rac</i> - 3c	DMSO	0.20	–0.93 (6.42)	–13.5 (116.3)	–8.3 (60.5)
2	<i>rac</i> - 3c	DMSO	0.02	–0.93 (6.42)	–13.5 (116.3)	–8.3 (60.5)
3	<i>rac</i> - 3c	DMSO ^[g]	0.20	–0.93 (6.41)	–13.6 (116.2)	–8.4 (60.4)
4	<i>rac</i> - 3b	DMSO	0.12	–0.93 (6.41)	–13.6 (116.2)	–8.4 (60.4)
5	<i>rac</i> - 3b	THF	0.21	–1.00 (6.34)	–13.3 (116.6)	–6.4 (62.4)
6	<i>rac</i> - 3d	DMSO	0.21	–0.92 (6.42)	–13.5 (116.3)	–8.3 (60.5)
7	<i>rac</i> - 3a	THF	0.34	–0.84 (6.50)	–11.2 (118.6)	–8.6 (60.2)
8	<i>rac</i> - 3a	THF ^[h]	0.31	–0.84 (6.50)	–11.1 (118.7)	–8.7 (60.1)
9	<i>rac</i> - 1b	THF	0.29	–1.1 to –1.3 ^[i] (6.16)	–12.4 to –15.6 ^[i] (114.2)	–4.3 (58.0)
10	<i>rac</i> - 1c	THF	0.10	–1.17 (6.18)	–15.0 (113.7)	–6.9 (53.0)
11	<i>rac</i> - 1d	THF	0.10	–1.17 (6.19)	–14.7 (114.0)	–5.8 (60.8)
12	(<i>M/P</i>)- 1d -2TMEDA	benzene	0.20	–0.24 ^[j] (6.81)	–13.7 ^[j] (114.8)	–7.2 ^[j] (59.4)
13	<i>rac</i> - 1f	THF	0.04	–0.52 (6.82)	–4.81 (123.3)	–14.0 (57.8)

[a] At room temperature. [b] $\Delta\delta = \delta_{\text{carbanion}} - \delta_{\text{sulfone}}$. [c] Sulfones were generally measured in CDCl₃. [d] Values of δ and $\Delta\delta$ [ppm]. [e] Deuterated solvent. [f] In mol L^{–1}. [g] In the presence of [2.2.2]cryptand. [h] In the presence of TMEDA. [i] Because of the uncertainty in the assignment of sulfone signal, only a signal range is given. [j] Sulfone in [D₆]benzene: $\delta(H_p) = 7.05$ ppm, $\delta(C_p) = 128.5$ ppm; and in CDCl₃: $\delta(H_p) = 7.36$ ppm, $\delta(C_p) = 128.7$ ppm.

of H_p and C_p for the (*S*)-trifluoromethylsulfonyl carbanion salts *rac*-**3a–c** and (*S*)-*tert*-butylsulfonyl carbanion salts *rac*-**1b–d**, and thus an increase in negative charge density at the *para* positions. On the basis of the $\Delta\delta X_p$ values, the prerequisites for a meaningful comparison of *rac*-**3a–c** and *rac*-**1b–d** are the existence of similar C_α–Ph and C_α–S conformations and coordination geometries of the C_α atoms. According to X-ray crystal structure analysis of monomers and dimers of the salts, these requisites are satisfactory met (see Table 7).^[3,5a,b] There is no good reason to believe that the CIPs

A further prerequisite for an analysis of the benzylic conjugation of salts *rac*-**3a–c** and *rac*-**1b–d** on the basis of the $\Delta\delta X_p$ values is the absence of a C_α–Li bond (for a discussion of the effect of a C_α–Li bond upon the *para* monitors, see below). This is, as discussed above and below, the case. The potassium (*S*)-trifluoromethylsulfonyl carbanion salt **3c** exhibited in [D₆]DMSO nearly identical chemical shifts for H_p, C_p, and C_α at different concentrations and in the presence of the potassium-ion-selective [2.2.2]cryptand (Table 9, entries 1–3).^[57] Therefore, the NMR spectroscopic parameters of *rac*-**3c** in [D₆]DMSO might be considered characteristic of the free carbanion and are not significantly influenced by ion-pairing effects. This is supported by the NMR spectroscopic parameters of the tetrabutylammonium salt *rac*-**3b** and tetramethylammonium salt *rac*-**3d** in [D₆]DMSO and [D₈]THF (Table 9, entries 4–6). The signals of H_p and C_p of the lithium salt *rac*-**3a** experience in [D₈]THF smaller upfield shifts than those of the potassium salt *rac*-**3c** in [D₆]DMSO (Table 9, entries 7 and 8). This is perhaps because of the Li-coordinated sulfonyl group, which is a stronger electron-attracting group than the free sulfonyl group

(see below).^[55a] As a consequence, charge transfer to the phenyl ring is lower in magnitude. Aside from these effects, there are no major differences in the pertinent NMR spectroscopic parameters of the potassium, tetraalkylammonium, and lithium salts. In summary, the $\Delta\delta H_p$ and $\Delta\delta C_p$ values of salts *rac-3a-c* and *rac-1b-d* (Table 9, entries 9–11) demonstrate a significant interaction of the negative charge with the phenyl group,^[55,58] and a comparison of the $\Delta\delta$ values of the α -(*S*)-trifluoromethyl- and α -(*S*)-*tert*-butylsulfonyl carbanion salts shows distinct differences.

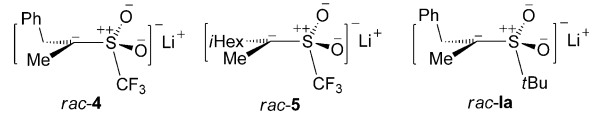
Generally, the $\Delta\delta H_p$ and $\Delta\delta C_p$ values are larger for the α -(*S*)-*tert*-butylsulfonyl than α -(*S*)-trifluoromethylsulfonyl carbanion salts. Although the differences are small, they indicate that the C atoms in the *para* position of the phenyl rings (C_p) of the (*S*)-trifluoromethylsulfonyl carbanion salts *rac-3a-c* have a lower negative charge density than the corresponding atoms of the (*S*)-*tert*-butylsulfonyl carbanion salts *rac-1b-d*. This conclusion is supported by ab initio calculations (see below). Thus, the benzylic interaction in the benzylic α -(*S*)-trifluoromethylsulfonyl carbanion salts *rac-3a-c*, which leads to a charge transfer to and/or polarization of the phenyl ring, is less than in the benzylic (*S*)-*tert*-butylsulfonyl carbanion salts *rac-1b-d*.

The values of the *para* monitors of the lithium salt *rac-1d* in $[D_8]THF$ are those of a mixture of monomers and dimers. Therefore, salt (*M/P*)-**1d**·2TMEDA was investigated in $[D_6]benzene$, in which it should exist exclusively as a dimer because of the low polarity and coordination solvation capacity of the solvent. The dimeric salt (*M/P*)-**1d**·2TMEDA was synthesized through deprotonation of the corresponding sulfone with *n*BuLi in *n*-hexane/TMEDA and recrystallization from TMEDA. Then the crystalline salt was dissolved in $[D_6]benzene$ and the solution subjected to NMR spectroscopy. Salt (*M/P*)-**1d**·2TMEDA in $[D_6]benzene$ and salt *rac-1d* in $[D_8]THF$ have very similar $\Delta\delta C_p$ values (Table 9, entries 11 and 12), which shows that the benzylic interactions in the monomer and dimer are similar. However, the $\Delta\delta H_p$ value of the dimer (*M/P*)-**1d**·2TMEDA in $[D_6]benzene$ (−0.24) is much smaller than that of the monomer/dimer mixture of *rac-1d* in $[D_8]THF$ (−1.17). This is most likely due to a downfield shift of the signal of H_p that is caused by the solvating $[D_6]benzene$ molecules, which are specifically orientated with their peripheral part towards the negatively charged phenyl ring of (*M/P*)-**1d**·2TMEDA.^[59] Similar downfield shifts were also recorded for the signals of H_p of the dimeric salts (*M/P*)-**1b**·4THF and (*M/P*)-**1c**·4THF in $[D_6]benzene$.^[3,53b]

The variation of the ^{13}C chemical shift ($\Delta\delta C_\alpha$) of the C atom (which bears the stabilizing group) of stabilized carbanions can yield qualitative information about the electronic reorganization that occurs during the ionization of the corresponding carbon acid.^[55] This variation is mainly the result of three effects: 1) the downfield shift caused by the $sp^3 \rightarrow sp^2$ rehybridization of the anionic C atom, 2) the upfield shift caused by the negative charge, and 3) the shift variation caused by a charge transfer to the stabilizing groups. Because of these partially opposing effects, the situa-

tion is complex, and it is generally difficult to reach a meaningful conclusion about the electronic changes on the basis of the $\Delta\delta C_\alpha$ value, which lacks information about the configurational and conformational reorganization. However, in the crystal phase the benzylic (*S*)-trifluoromethylsulfonyl carbanion salt *rac-3a* and *rac-3b*, and the (*S*)-*tert*-butylsulfonyl carbanion salts *rac-1c* and *rac-1d* are all endowed with planar C_α atoms and similar $C_\alpha-Ph$ and $C_\alpha-S$ conformations. Therefore, it can be assumed with confidence that salts *rac-3a-c* and *rac-1b-d* have planar C_α atoms and similar $C_\alpha-Ph$ and $C_\alpha-S$ conformations in solution. Table 10 shows that de-

Table 10. Selected NMR spectroscopic data of the dialkyl-substituted (*S*)-trifluoromethylsulfonyl carbanion salts *rac-4*, and *rac-5*, and (*S*)-*tert*-butylsulfonyl carbanion salt *rac-1a*.^[a-d]



Salt	Solvent ^[e]	<i>c</i> [mol L ^{−1}]	$\Delta\delta C_\alpha$ (δC_α)
<i>rac-4</i>	THF	0.29	−13.8 (44.8)
<i>rac-5</i>	diglyme	0.52	−13.5 (44.2)
<i>rac-1a</i>	THF	0.31	−17.4 (37.9)

[a] At room temperature. [b] $\Delta\delta = \delta_{\text{carbanion}} - \delta_{\text{sulfone}}$. [c] Sulfones in $CDCl_3$. [d] Values of δ and $\Delta\delta$ [ppm]. [e] Deuterated.

spite the complete $sp^3 \rightarrow sp^2$ rehybridization of the anionic C atom, which generally makes a large positive contribution to $\Delta\delta C_\alpha$,^[55] the $\Delta\delta C_\alpha$ values of salts *rac-3a-c* and *rac-1b-d* are negative. These results are compatible with only a minor charge transfer to the sulfonyl group and the confinement of the negative charge of both types of salts, mainly to the anionic C atoms.^[9,55] The differences in the $\Delta\delta C_\alpha$ values of salts *rac-3a-c* and *rac-1b-d* indicate a slightly higher negative charge density at the C_α atoms of the α -(*S*)-trifluoromethylsulfonyl carbanion salts, this being perhaps the result of the reduced benzylic interaction. On the basis of the acidity of $ArCH_2SO_2R$ ($R=Ph, CF_3$)^[60] and reactivity of $[ArCH-SO_2R]^-$ ($R=Ph, CF_3$)^[10b] it was proposed that the anionic C atoms of the (*S*)-trifluoromethylsulfonyl carbanions carry a lower negative charge density than those of the (*S*)-phenylsulfonyl carbanions.

The $\Delta\delta C_\alpha$ values of −13.5 to −17.4 ppm of the dialkyl-substituted (*S*)-trifluoromethylsulfonyl carbanion salts *rac-4* and *rac-5*, and the (*S*)-*tert*-butylsulfonyl carbanion salt *rac-1a* (Table 10) fit into the picture of a high negative charge density at the C_α atom. The $\Delta\delta C_\alpha$ values of these salts are more negative than those of the benzylic salts because of the lack of a charge transfer to the phenyl group as in *rac-3a-c* and *rac-1b-d* (see Table 9, entry 12). Although X-ray crystal structure analyses of salts *rac-4*, *rac-5*, and *rac-1a* are not available, their C_α atoms are perhaps slightly pyramidalized (see below).^[3]

para Monitors and CIP structures: The *para* monitors of salts *rac-3a-c* and *rac-1b-d* also yield information about the structure of their CIPs. For example, should the lithium salt

rac-3a in THF/TMEDA predominantly exist as CIP **3aC**, then its $\Delta\delta H_p$ and $\Delta\delta C_p$ values should be smaller than those of the corresponding ammonium salt *rac-3b* and potassium salt *rac-3c*. Because of the C_α -Li bond in **3aC**, charge transfer to and/or polarization of the phenyl ring at the C_α atom will be diminished relative to *rac-3b* and *rac-3c*. This notion is supported by ab initio calculations (see below). Experimentally, such an effect of the C_α -Li bond had been demonstrated for lithiated benzylic sulfanes by NMR spectroscopy of their CIPs and solvent-separated ion pairs (SIPs).^[61] It should be noted, however, that the magnitude of this effect for lithiated sulfones is difficult to delineate because of the lack of information about the $\Delta\delta H_p$ and $\Delta\delta C_p$ values for CIPs of type **C**. The similarity of the $\Delta\delta H_p$ and $\Delta\delta C_p$ values for the phenyl group of the lithium salt *rac-3a*, potassium salt *rac-3c*, and tetrabutylammonium salt *rac-3b* speaks (see above) against the existence of **3aC** and for **3aA** and **3aB** as the dominating species.

In accordance with this reasoning are the results of a previous NMR spectroscopic study on the pairs of the benzylic (*S*)-*tert*-butylsulfonyl carbanion salts *rac-1b*·(THF)_m and *rac-1b*·12c4, *rac-1c*·(THF)_m and *rac-1c*·PMDTA, and the allylic salts *rac-1e*·(THF)_m and *rac-1e*·PMDTA in [D₈]THF (see Figure 15).^[3,40] From the perspective of the ligands of the Li atom, salts *rac-1b*, *rac-1c*, and *rac-1e* can in principle form with the monodentate ligand [D₈]THF all three CIP types, **A–C**. In contrast, with the tridentate ligand PMDTA and the tetradentate ligand 12c4, the salts are expected to form the CIP type **B** because of the availability of only one coordination at the Li atom for the carbanion. According to X-ray crystal structure analyses of *rac-1b*·12c4, *rac-1c*·PMDTA and *rac-1e*·PMDTA, the carbanions are coordinated through one O atom to the Li atom.^[5] Only minor differences were recorded for the $\Delta\delta H_p$, $\Delta\delta C_p$, $\delta(=H_2)$, and $\Delta\delta(=CH_2)$ values of the C_α -Ph and the =CH₂ group of the respective carbanions in the pairs of salts. This was taken as an indication for the existence of salts *rac-1b*, *rac-1c*, and *rac-1e* in [D₈]THF as CIPs of type **A** and **B** but not **C**. As discussed above, the CIPs **C** of salts *1b*·(THF)_m, *rac-1c*·(THF)_m, and *rac-1e*·(THF)_m should differ in their $\Delta\delta H_p$, $\Delta\delta C_p$, $\Delta\delta(=CH_2)$, and $\Delta\delta(=CH_2)$ values, respectively, from the corresponding salts *rac-1b*·12c4, *rac-1c*·PMDTA, and *rac-1e*·PMDTA because of a reduced benzylic and allylic charge transfer due to the C_α -Li bond.^[61] Furthermore, the close similarities in the pertinent NMR spectroscopic data of the CIP *rac-1c*·(THF)_m in [D₈]THF and those of a 7:3 mixture of the SIP *rac-1c*/Li(HMPA)₄ and CIP *rac-1c*·(THF)_m in [D₈]THF are also more compatible with the existence of *rac-1c*·(THF)_m as CIPs of type **A** and **B** rather than **C**.^[3,53c]

In addition to the *para* monitors of salt *rac-3a*, the $\Delta\delta C_\alpha$ values also give information about the structure of its CIPs. An inspection of Table 9 shows that salt *rac-3a* has in THF/TMEDA (Table 9, entry 8) and in THF (Table 9, entry 7) almost the same $\Delta\delta C_\alpha$ value as the ammonium salt *rac-3b* (Table 9, entry 4) and potassium salt *rac-3c* (Table 9, entry 1) in DMSO. This can be taken as further evidence that the lithium salt preferentially exists as CIPs **3aA** and/or

3aB and not CIP **3aC**. The C_α -Li bond of **3aC** would result in a higher negative charge density at the anionic C atom because of the reduced charge transfer to the phenyl ring relative to *rac-3b* and *rac-3c* (see below). Hence, the $\Delta\delta C_\alpha$ value of **3aC** should be more negative than the values of the corresponding ammonium and potassium salts.^[61]

Structure of α -(*S*)-trifluoromethyl- and α -(*S*)-*tert*-butylsulfonyl carbanions in the gas phase:

The studies of the lithium salts **I** and **II** showed that, relative to the (*S*)-*tert*-butylsulfonyl group, the (*S*)-trifluoromethylsulfonyl group 1) reduces the ability of the lone pair to engage in C–C bond formation, 2) diminishes the interaction of the negative charge with the phenyl group, and 3) enhances the C_α -S rotational barrier. To gain a deeper understanding of the differences in the electronic structure of the benzylic α -(*S*)-trifluoromethylsulfonyl and α -(*S*)-*tert*-butylsulfonyl carbanions of the type studied in this work, ab initio calculations were carried out on the counterion-free (*S*)-*tert*-butylsulfonyl carbanion **XI** and (*S*)-trifluoromethylsulfonyl carbanion **XII**, and the corresponding sulfones **59** and **60** (Figure 16). All calcula-

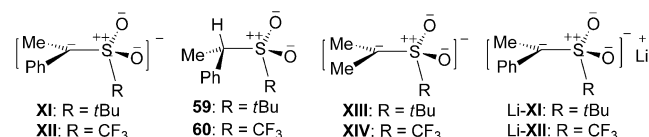


Figure 16. α -(*S*)-*tert*-Butylsulfonyl and α -(*S*)-trifluoromethylsulfonyl carbanions and sulfones.

tions of **XI**, **XII**, **59**, and **60** were performed using the program Gaussian 09.^[62] The structures were optimized at the MP2 level of theory^[63] by employing the 6-31+G*^[64] set of contracted Gaussian functions. The resulting structures are shown in Figures 17–19. Tables 11–13 and Table S17 in the

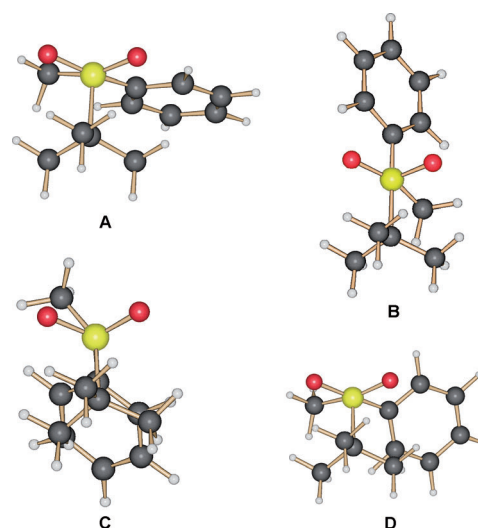


Figure 17. View of the calculated structures of conformers **A–D** of the (*S*)-*tert*-butylsulfonyl carbanion **XI**. Color code: C, black; S, yellow; O, red; H, gray.

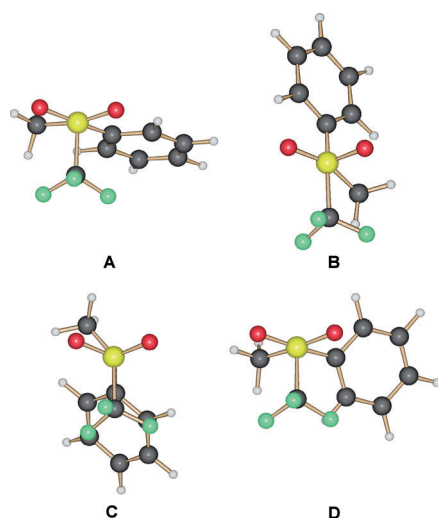


Figure 18. View of the calculated structures of conformers **A–D** of the (*S*)-trifluoromethylsulfonyl carbanion **XII**. Color code: C, black; S, yellow; O, red; F, green; H, gray.

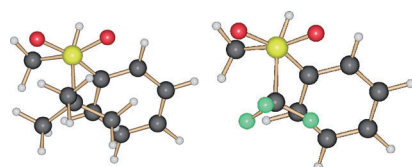


Figure 19. View of the calculated structures of *tert*-butylsulfone **59** (left) and triflone **60** (right). Color code: C, black; S, yellow; O, red; F, green; H, gray.

Table 11. Total energies of the conformers **A–D** of the (*S*)-*tert*-butylsulfonyl carbanion **XI** and (*S*)-trifluoromethylsulfonyl carbanion **XII**, and sulfones **58** and **59** [hartree].^[a]

Conformer	XI	XII
A	–1013.606358 (0.268185)	–1193.199273 (0.158409)
B	–1013.582818	–1193.176716
C	–1013.576615	–1193.170212
D	–1013.589258	–1193.190527
	59	60
	–1014.178486 (0.283776)	–1193.748663 (0.173070)

[a] The numbers in parentheses are zero-point energies. No zero-point energies are given for conformers that do not correspond to minimum structures (MP2/6-31+G*; 1 hartree/particle = 627.5095 kcal mol^{–1}).

Supporting Information contain information about their energies and bonding parameters.

We had previously studied the C_α–S rotation of the (*S*)-*tert*-butylsulfonyl carbanion **XI** by ab initio calculations.^[3] Carbanion **XI** was found to have a planar C_α atom and similar C_α–Ph and C_α–S conformations to the corresponding lithium salt *rac*-**Ic**·PMDTA in the crystal phase.^[4] In addition, we investigated the non-benzylic analogues, the α -sulfonyl carbanions **XIII** and **XIV**, by ab initio and NBO calculations.^[3] The (*S*)-*tert*-butylsulfonyl carbanion **XIII** ($\Sigma(\angle(C_{\alpha}))=356.1^{\circ}$) and the (*S*)-trifluoromethylsulfonyl car-

Table 12. Selected structural parameters, relative energies (ΔE_{rel}), and details of the NBO analyses of the α -sulfonyl carbanions **XIA** and **XIIA**.^[a,b]

Parameter/Energy	XIA	XIIA
ΔE_{rel}	0.00 ^[c]	0.00 ^[d]
S–R	1.886	1.887
S–C _α	1.695	1.665
C _α –Ph	1.441	1.456
$\Sigma(\angle(C_{\alpha}))$	357.89	356.26
$n(\sigma_{\text{S–R}}^*)$	0.2039	0.3049
$\epsilon(\sigma_{\text{S–R}}^*)$	0.4673	0.3693
$n(\sigma_{\text{S–R}})$	1.9559	1.9582
$\epsilon(\sigma_{\text{S–R}})$	–0.6472	–0.7044

[a] Relative energies [kcal mol^{–1}], bond lengths [\AA], bond angles [$^{\circ}$], occupation number n [e], and orbital energies ϵ [hartree]. [b] All values are at the MP2/6-31+G* level. [c] $\Delta E_{\text{prot}} = -349.23$ kcal mol^{–1}. [d] Energy of protonation (ZPE + MP2/6-31+G*): $\Delta E_{\text{prot}} = -335.55$ kcal mol^{–1}.

Table 13. Stereoelectronic effects of the conformers **A** of carbanions **XI** and **XII** [kcal mol^{–1}].

Interaction	XIA	Interaction	XIIA
$\sigma_{\text{O–S}} \rightarrow \sigma_{\text{S–tBu}}^*$	2.6	$\sigma_{\text{O–S}} \rightarrow \sigma_{\text{S–CF}_3}^*$	4.9
$\sigma_{\text{S–O}} \rightarrow \sigma_{\text{S–tBu}}^*$	2.4	$\sigma_{\text{S–O}} \rightarrow \sigma_{\text{S–CF}_3}^*$	4.7
$\sigma_{\text{S–C}} \rightarrow \sigma_{\text{S–tBu}}^*$	1.2	$\sigma_{\text{S–C}} \rightarrow \sigma_{\text{S–CF}_3}^*$	1.3
$\sigma_{\text{S–C}_{\alpha}} \rightarrow \sigma_{\text{S–tBu}}^*$	2.2	$\sigma_{\text{S–C}_{\alpha}} \rightarrow \sigma_{\text{S–CF}_3}^*$	3.8
$\sigma_{\text{CH}} \rightarrow \sigma_{\text{S–tBu}}^*$	4.1	$n_{\text{F}} \rightarrow \sigma_{\text{S–CF}_3}^*$	0.5, 7.4, 0.7, 8.0, 0.6, 7.6
$n_{\text{O}} \rightarrow \sigma_{\text{S–tBu}}^*$	17.4	$n_{\text{O}} \rightarrow \sigma_{\text{S–CF}_3}^*$	16.8
$n_{\text{O}} \rightarrow \sigma_{\text{S–tBu}}^*$	4.3	$n_{\text{O}} \rightarrow \sigma_{\text{S–CF}_3}^*$	12.1
$n_{\text{O}} \rightarrow \sigma_{\text{S–tBu}}^*$	17.1	$n_{\text{O}} \rightarrow \sigma_{\text{S–CF}_3}^*$	14.5
$n_{\text{O}} \rightarrow \sigma_{\text{S–tBu}}^*$	4.7	$n_{\text{O}} \rightarrow \sigma_{\text{S–CF}_3}^*$	14.8
$n_{\text{C}_{\alpha}} \rightarrow \sigma_{\text{S–tBu}}^*$	28.9	$\pi_{\text{C}_{\alpha}\text{–Ph}} \rightarrow \sigma_{\text{S–CF}_3}^*$	33.1

banion **XIV** ($\Sigma(\angle(C_{\alpha}))=354.1^{\circ}$) have slightly pyramidalized C_α atoms. Whereas the (*S*)-trifluoromethylsulfonyl carbanion **XIV** carries a lone pair at the C_α atom with an occupation number $n=1.6129$ e and with about 95% p character, there is, according to an NBO analysis,^[65] none at the C_α atom of the (*S*)-*tert*-butylsulfonyl carbanion **XIII** but rather a S–C_α π bond instead. However, almost 90% of this bond is located at the C_α atom, which can therefore be considered a lone pair. Furthermore, the hybrid at the carbon atom is an almost pure p orbital, whereas the one at sulfur has up to 36% d character. The participation of d orbitals on the S atom in the S–C_α π bond of **XIII** is interesting. Previous theoretical studies of [CH₂SO₂Me][–] had given no indication for the involvement of d orbitals on the S atom in the stabilization of the carbanion.^[41,66] Although the energy associated with the $n_{\text{C}_{\alpha}} \rightarrow \sigma_{\text{S–CF}_3}^*$ interaction in **XIV** is $\Delta E_2 = -65.9$ kcal mol^{–1}, the energy that results from the $\pi_{\text{S–C}_{\alpha}} \rightarrow \sigma_{\text{S–tBu}}^*$ interaction in **XIII** amounts only to $\Delta E_2 = -43.8$ kcal mol^{–1}. The fully optimized structures of the benzylic (*S*)-*tert*-butylsulfonyl carbanion **XIA** and (*S*)-trifluoromethylsulfonyl carbanion **XIIA** as well as those of the (*S*)-*tert*-butyl sulfone **59** and triflone **60** are local minima with exclusively real frequencies in the spectra of their normal modes. One measure of the stabilization of the negative charge in carbanions **XIA** and **XIIA** is the energy required to remove the acidic proton from the C_α atom of the corresponding sulfones **59**

and **60**, or, conversely, the protonation energy of the carbanions. The calculated energy of protonation^[62] for **XIIA** is $-335.6 \text{ kcal mol}^{-1}$, whereas addition of a proton to **XIA** yields $-349.6 \text{ kcal mol}^{-1}$. Therefore, as a rough estimate the negative charge of the α -(*S*)-trifluoromethylsulfonyl carbanion appears to be stabilized by about 15 kcal mol^{-1} more effectively than the one of the α -(*S*)-*tert*-butylsulfonyl carbanion. Examination of both carbanions **XIA** and **XIIA** with an antiperiplanar orientation of the lone pair at the C_α atom and the group R (CF_3 , *t*Bu), and an orthogonal alignment of the lone pair and the plane of the phenyl rings reveals that these structures are ideal for a twofold stabilization of a presumed anionic lone pair by 1) hyperconjugative interaction with the σ^* orbital of the S–R bond ($\text{R} = \text{CF}_3$, *t*Bu), and 2) benzylic conjugation with the π system of the phenyl ring, thereby resulting in a charge transfer to the latter.

Anionic hyperconjugation: To study the role of anionic hyperconjugation in both carbanions we also generated structures for the conformers **XIB**, **XIC**, **XIIB**, and **XIIC**, in which the lone pair and the substituent R are either in a synclinal (**B**) or anticlinal (**C**) orientation, and therefore such an interaction between a lone pair at the C_α atom and the σ^* orbital of the S–R bond would not be possible. For that purpose we started from the fully optimized structures and fixed the dihedral angle $\theta(\text{R-S-C}_\alpha\text{-Ph})$ at 180° (**XIB**, **XIIB**) or 0° (**XIC**, **XIIC**), whereas all remaining structural parameters were optimized without any further constraints. The obtained conformers **XIB** and **XIIB** are 14.8 and $14.2 \text{ kcal mol}^{-1}$ energetically above the local minima **XIA** and **XIIA**. Because of the eclipsed orientation of the phenyl group and substituent R, the conformers **XIC** and **XIIC** are even higher in energy (18.7 and $18.2 \text{ kcal mol}^{-1}$). At this level of approximation we therefore expected a twofold barrier towards rotation about the C_α –S bond with only slightly higher maxima for the α -(*S*)-trifluoromethylsulfonyl carbanion. In the following discussion, we will only refer to **XIA** and **XIIA**. The obtained wave functions of **XIA** and **XIIA** were then subjected to an NBO analysis.^[65] These NBO calculations gave a lone pair with an occupation number of $n = 1.5905 \text{ e}$ at the C_α atom of the (*S*)-*tert*-butylsulfonyl carbanion **XIA**, which is linked to the phenyl group by a single bond. No such lone pair at the C_α atom was obtained for the (*S*)-trifluoromethylsulfonyl carbanion **XIIA**. Unlike **XIA**, the NBO analysis for **XIIA** produced an additional π bond with an occupation number of $n = 1.7653 \text{ e}$ between the C_α atom and the phenyl group. However, like the S– C_α π bond in the nonbenzylic (*S*)-*tert*-butylsulfonyl carbanion **XIII**, this bond in **XIIA** is strongly polarized and localized to about 82% at the formally anionic C atom so that it can be considered a lone pair.^[3] The energy associated with the interaction of this π orbital with the S– CF_3 antibond ($\pi_{C_\alpha\text{-Ph}} \rightarrow \sigma^*_{\text{S-CF}_3}$) in **XIIA** is $\Delta E_2 = -33.1 \text{ kcal mol}^{-1}$, whereas the energy that results from the $n_{\text{C}} \rightarrow \sigma^*_{\text{S-}t\text{Bu}}$ interaction in the (*S*)-*tert*-butylsulfonyl carbanion **XIA** amounts to $\Delta E_2 = -28.9 \text{ kcal mol}^{-1}$. Thus, the stabilization of the negative charge of **XIIA** by the interaction of the strongly polarized C_α –Ph π bond

with $\sigma^*_{\text{S-CF}_3}$ is more effective than the stabilization of **XIA** by the $n_{\text{C}} \rightarrow \sigma^*_{\text{S-}t\text{Bu}}$ interaction. Since the presence of a lone pair at the C_α atom will facilitate an electrophilic attack at this center, we conclude that the α -(*S*)-trifluoromethylsulfonyl carbanion should be less prone to undergo electrophilic capture at the anionic C atom than the α -(*S*)-*tert*-butylsulfonyl carbanion.

The addition of all second-order energies of interaction (ΔE_2) between the $\sigma^*_{\text{S-R}}$ orbitals in **XIA** and **XIIA** and all occupied NBOs resulted in an approximately 38 kcal mol^{-1} more favorable value for the α -(*S*)-trifluoromethylsulfonyl carbanion than for the α -(*S*)-*tert*-butylsulfonyl carbanion. In particular, the $n_{\text{O}} \rightarrow \sigma^*_{\text{S-R}}$ interactions in the α -(*S*)-trifluoromethylsulfonyl carbanion are more energy lowering than in the α -(*S*)-*tert*-butylsulfonyl carbanion. The more effective interactions in the case of **XIIA** correlate with the different energies of the $\sigma^*_{\text{S-R}}$ orbitals in both carbanions, which are 0.3693 hartree in **XIIA** and 0.4673 hartree in **XIA**. This is also reflected by the occupation numbers n of the $\sigma^*_{\text{S-R}}$ orbitals, which are 0.3049 e for the α -(*S*)-trifluoromethylsulfonyl and 0.2039 e for the α -(*S*)-*tert*-butylsulfonyl carbanion. These results emphasize the role of the S–R antibonds in the stabilization of the carbanions. Whereas in the case of the (*S*)-*tert*-butylsulfonyl carbanion **XIA** a lone-pair orbital at the C_α atom contributes to this process, the loss of stabilization owing to lack of such an orbital in the (*S*)-trifluoromethylsulfonyl carbanion **XIIA** is outnumbered by cumulatively more favorable interactions with other occupied orbitals including the $\pi_{C_\alpha\text{-Ph}} \rightarrow \sigma^*_{\text{S-CF}_3}$ and $n_{\text{O}} \rightarrow \sigma^*_{\text{S-CF}_3}$ interactions.

It is interesting to compare **XIA** and **XIIA** with the unsubstituted (*S*)-methylsulfonyl carbanion **III** and (*S*)-trifluoromethylsulfonyl carbanion **IV** (see Figure 1), which we had previously studied.^[6] As expected, both have a lone pair of 91–93% p character at the C_α atom with a slightly higher occupation number of $n = 1.8082 \text{ e}$ for **III** than with $n = 1.7169 \text{ e}$ for **IV**, thus indicating a stronger mixing with the $\sigma^*_{\text{S-R}}$ orbital for the (*S*)-trifluoromethylsulfonyl carbanion. This is also reflected by a higher occupation number of $\sigma^*_{\text{S-R}}$ in **IV** (0.3160 e) than in **III** (0.1958 e) and a significantly more negative ΔE_2 for the $n_{\text{C}} \rightarrow \sigma^*_{\text{S-R}}$ interaction in the former ($-54.2 \text{ kcal mol}^{-1}$) than in the latter carbanion ($-34.2 \text{ kcal mol}^{-1}$). At first glance, the different occupation numbers of the $\sigma^*_{\text{S-R}}$ orbitals in the benzylic sulfonyl carbanions provide an explanation for the differences in the S–R bond length, which are 1.887 \AA in **XIIA** and 1.866 \AA in **XIA**. However, these bond lengths are the same as in conformers **XIIB** (1.887 \AA) and **XIB** (1.866 \AA), for which the occupation numbers of the corresponding antibonding orbitals are significantly lower (**XIIB**: 0.2374 e , **XIB**: 0.1607 e), whereas those of the bonding $\sigma_{\text{S-R}}$ orbitals are very similar (**XIIB**: 1.9598 e , **XIB**: 1.9603 e) to those in **XIIA** (1.9582 e) and **XIA** (1.9559 e). Therefore, it appears that within the framework of the NBO method the occupation number of an antibond does not necessarily correlate with the corresponding bond length. The lower occupation numbers of the $\sigma^*_{\text{S-R}}$ orbitals of the **B** conformers indicate a less favorable

ΔE_2 for **XIB** and **XIIB**. And indeed, relative to **XIIA** and **XIA**, the total second-order stabilization energies between the σ^*_{S-R} orbitals and occupied NBOs are 13–20 kcal mol⁻¹ less favorable in **XIIB** and **XIB**. Moreover, at a difference of approximately 46 kcal mol⁻¹ between **XIIB** and **XIB**, these interactions are more favorable for the α -(*S*)-trifluoromethylsulfonyl than for the α -(*S*)-*tert*-butylsulfonyl carbanion, such as in the case of **XIIA** and **XIA**. Again, the occupation number of the σ^*_{S-R} orbital in **XIB** (0.1607 e) is lower than in **XIIB** (0.2374 e), which corresponds to a lower orbital energy for the α -(*S*)-trifluoromethylsulfonyl carbanion (0.3667 hartree) than for the α -(*S*)-*tert*-butylsulfonyl carbanion (0.4656 hartree).

According to the NBO analyses, the hyperconjugative interaction of the lone pair at the C _{α} atom with the σ^*_{S-R} orbital in the (*S*)-*tert*-butylsulfonyl carbanion **XIA** (–28.9 kcal mol⁻¹) is only about one-third of its interaction with a π^* orbital of the phenyl ring (–98.4 kcal mol⁻¹, $n = 0.4120$ e). The energetically most favorable interactions between the π component of the polarized double bond between the C _{α} atom and phenyl ring and two π^* orbitals of the ring in the α -(*S*)-trifluoromethylsulfonyl carbanion **XIIA** amount to about –8.0 kcal mol⁻¹, and are therefore much weaker. In sulfones **58** (S-*t*Bu: 1.865 Å; CH-S: 1.695 Å) and **59** (S-CF₃: 1.887 Å; CH-S: 1.665 Å), the C _{α} -H σ bonds are in an almost ideal orientation to interact hyperconjugatively with the σ^*_{S-R} antibonding orbitals. However, these interactions are only –3.0 and –2.5 kcal mol⁻¹ for **58** and **59**, respectively, and are therefore relatively weak.

Benzylic conjugation: To further evaluate the role of the benzylic stabilization, we optimized the structures of the two additional conformers **XID** and **XIID**. In these optimizations, the orientation of the phenyl group was fixed in a position in which the lone-pair orbital lies approximately in the plane of the ring and benzylic conjugation is thus widely shut off. Whereas in the case of the (*S*)-*tert*-butylsulfonyl carbanion **XI** the energy difference between the **A** and the **D** conformers amounts to 10.7 kcal mol⁻¹, it is only 5.5 kcal mol⁻¹ for the α -(*S*)-trifluoromethylsulfonyl carbanion **XII**. We therefore conclude that the benzylic conjugation is almost two times more stabilizing in the (*S*)-*tert*-butylsulfonyl carbanion **XI** (–10.7 kcal mol⁻¹) than in the (*S*)-trifluoromethylsulfonyl carbanion **XII** (–5.5 kcal mol⁻¹). The phenyl rings of both carbanions **XI** and **XII** carry negative natural charges. The values including the hydrogen atoms are –0.1633 e for the (*S*)-trifluoromethylsulfonyl carbanion **XIIA** and –0.2403 e for the (*S*)-*tert*-butylsulfonyl carbanion **XIA**. In particular, the negative charge of C_p in **XIA** is –0.3559 e and in **XIIA** –0.3234 e. If the hydrogen atoms are omitted from summation of the charges, the values are –1.3024 and –1.3647 e for **XIIA** and **XIA**, respectively. These computational results qualitatively correspond to those obtained experimentally by NMR spectroscopy (see above) and show that benzylic conjugation is somewhat stronger in the (*S*)-*tert*-butylsulfonyl carbanion **XIA** than in the α -(*S*)-trifluoromethylsulfonyl carbanion **XIIA**.

Structure of lithium α -(*S*)-trifluoromethylsulfonyl and α -(*S*)-*tert*-butylsulfonyl carbanion salts in the gas phase: Previous ab initio calculations of solvated lithium α -sulfonyl carbanion salts gave all three types of CIPs, **A–C** (see Figure 13), as energy-minimum structures, depending on the ligands of the Li atom. Salts [MeC(H)SO₂Ph]Li·2Me₂O^[51a] and [PhC(H)SO₂Ph]Li·2Me₂O,^[67] both of which carry two ether molecules at the Li atom, adopt the O₂C _{α} Li structure **C**. In contrast, salt [PhC(H)SO₂Ph]Li·3Me₂O, which has three ether molecules coordinated to the Li atom, prefers the O₂Li structure **B**.^[67] The allylic salt [CH₂=CHC(H)SO₂Ph]Li·2 THF assumes the O₂Li, O and O₂C _{α} Li structures **A** and **C**, respectively, with the same energy.^[68] Finally, the benzylic salt [PhC(H)SO₂Ph]Li·L*, which carries a chiral bidentate bis-oxazoline ligand at the Li atom, has the O₂Li, O structure **A**.^[14] However, all these solvated lithium α -sulfonyl carbanion salts carry only one substituent at the anionic C and a phenyl group at the S atom. Therefore, we carried out ab initio calculations of the monomeric lithium (*S*)-*tert*-butylsulfonyl salt Li-**XI**·2Me₂O and lithium (*S*)-trifluoromethylsulfonyl salt Li-**XII**·2Me₂O, both of which bear two substituents at the C _{α} atom and two Me₂O molecules at the Li atom (Figure 20). Dimethyl ether was selected as the

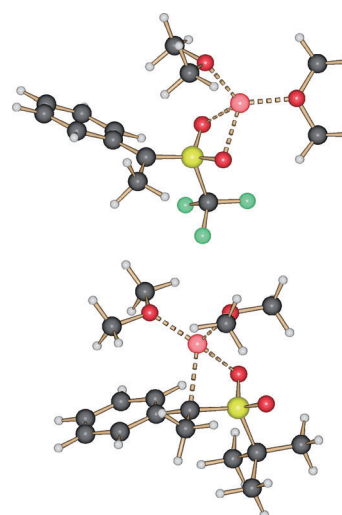


Figure 20. View of the calculated structures of the lithium (*S*)-trifluoromethylsulfonyl carbanion salt Li-**XII**·2Me₂O (top) and lithium (*S*)-*tert*-butylsulfonyl carbanion salt Li-**XI**·2Me₂O (bottom). Color code: C, black; S, yellow; O, red; Li, pink; F, green; H, gray.

ligand for the Li atom since ab initio calculations of [PhC(H)SO₂Ph]Li·(Me₂O)_{*m*} had shown this ligand to be an appropriate substitute for THF.^[67] Our ab initio geometry optimizations (MP2/6-31+G*) of the monomeric salts Li-**XII**·2Me₂O and Li-**XI**·2Me₂O gave a structure for the trifluoromethylsulfonyl salt in which the Li atom is coordinated to both O atoms (O–Li = 2.055 and 2.067 Å) and the O···Li···O plane approximately bisects the O–S–O angle. Consequently, both S–O bonds have about the same length (1.505 and 1.510 Å, respectively). In the *tert*-butylsulfonyl

salt Li-**XI**·2Me₂O, the Li atom is coordinated by only one O atom (O–Li=2.008 Å) in addition to the C_α atom (C_α–Li=2.295 Å), thereby resulting in different S–O bond lengths of 1.512 Å (coordinating) and 1.493 Å. Although the length of the C_α–S bond of salt Li-**XII**·2Me₂O is shorter than that of the corresponding free carbanion **XIIA**, salt Li-**XI**·2Me₂O has a slightly longer C_α–S bond than the corresponding free carbanion **XIA** (Table 14). Furthermore, the

Table 14. Bond angles [°], bond lengths [Å], and dihedral angles [°] of salts Li-**XI**·2Me₂O and Li-**XII**·2Me₂O.

Parameter	Li- XI ·2Me ₂ O	Li- XII ·2Me ₂ O
C _α –S	1.710	1.635
C _α –Ph	1.470	1.467
S–R	1.847	1.885
C _α –Li	2.295	–
O–Li	2.008	2.055, 2.067
Σ[<(C _α)]	353.1	359.3
C _i –C _α –S–C	–62.7	–90.4
C _o –C _i –C _α –S	155.0, –30.3	–162.6, 16.8
Li–C _α –C _i –C _o	–123.3, 56.2	–
Me–C _α –S–C	87.7	80.0

lengths of the C_α–Ph bonds of the salts are longer than those of the corresponding free carbanions. Whereas the anionic C atom of the *tert*-butylsulfonyl salt Li-**XI**·2Me₂O is slightly pyramidalized, that of the trifluoromethylsulfonyl salt Li-**XII**·2Me₂O is planar. Thus, there is a good agreement between the theoretical and experimental results with regard to the planarity of the C_α atoms of the benzylic salts *rac*-**3a**, *rac*-**3b**, and Li-**XII**·2Me₂O. Both salts Li-**XI**·2Me₂O and Li-**XII**·2Me₂O have similar C_α–S conformations despite the presence of a C_α–Li bond in the former salt. Unlike carbanions **XIA** and **XIIA**, the anionic parts of both salts have a lone pair at the C_α atom with occupation numbers of 1.5448 e for the trifluoromethylsulfonyl salt Li-**XII**·2Me₂O and 1.6635 e for the *tert*-butylsulfonyl salt Li-**XI**·2Me₂O. The difference between these occupation numbers suggest a stronger mixing of the lone pair with the σ*_{S–R} antibonding orbital for Li-**XII**·2Me₂O than for Li-**XI**·2Me₂O. This assumption is supported by the second-order n_C→σ*_{S–R} interaction energies, which are –64.5 kcal mol^{–1} for Li-**XII**·2Me₂O and only –27.1 kcal mol^{–1} for Li-**XI**·2Me₂O. Consequently, the occupation numbers of the σ*_{S–R} orbitals are n=0.3259 e in the former and n=0.1892 e in the latter case. Relative to carbanions **XIA** and **XIIA**, there is therefore a much stronger hyperconjugative interaction with the orbital at the C_α atom in the trifluoromethylsulfonyl salt Li-**XII**·2Me₂O. Generally, the second-order n_C→σ*_{S–R} interaction energies of α-sulfonyl carbanions and their lithium salts are larger for R=CF₃ than for R=Me and *t*Bu (Table 15). The absolute values of the negative charges of the phenyl rings of the Li salts Li-**XI**·2Me₂O and Li-**XII**·2Me₂O are lower than those for the corresponding carbanions **XI** and **XII**; that is, –0.0677 e for the trifluoromethylsulfonyl salt Li-**XII**·2Me₂O and –0.1320 e for the *tert*-butylsulfonyl salt Li-**XI**·2Me₂O. By omitting the hydrogen atoms from the summation, we obtained a negative charge of –1.2441 e for

Table 15. Second-order n_C→σ*_{S–R} interaction energies of α-sulfonyl carbanions according to NBO calculations [kcal mol^{–1}].

Carbanion/Carbanion salt	ΔE
[CH ₂ SO ₂ Me] [–] (III)	–34.2 ^[a]
[CH ₂ SO ₂ CF ₃] [–] (IV)	–54.2
[MeC(Me)SO ₂ Me] [–]	–35.1 ^[b]
[MeC(Me)SO ₂ <i>t</i> Bu] [–] (XIII)	–43.8
[MeC(Me)SO ₂ CF ₃] [–] (XIV)	–65.9
[PhC(Me)SO ₂ <i>t</i> Bu] [–] (XI)	–28.9
[PhC(Me)SO ₂ CF ₃] [–] (XII)	–33.1 ^[c]
[PhC(H)SO ₂ CF ₃][Li·L] ^{*[d]}	–56.2 ^[e]
[PhC(Me)SO ₂ <i>t</i> Bu]Li·2Me ₂ O (Li- XI ·2Me ₂ O)	–27.1
[PhC(Me)SO ₂ CF ₃]Li·2Me ₂ O (Li- XII ·2Me ₂ O)	–64.5

[a] Ref. [68]. [b] Ref. [3]. [c] π_{C_α–Ph}→σ*_{S–CF₃}. [d] L*=(4*S*,4'*S*)-2,2'-(propane-2,2'-diyl)bis(4-phenyl-4,5-dihydrooxazole). [e] Ref. [14].

Li-**XII**·2Me₂O and –1.3160 e for Li-**XI**·2Me₂O. Similar to the free carbanions, the C_p atoms carry the strongest negative charge among the ring atoms (–0.2815 e and –0.3082 e, respectively).

Conclusion

Lithium α-(*S*)-trifluoromethylsulfonyl carbanion salts are not only more stable and less nucleophilic than the corresponding α-(*S*)-*tert*-butylsulfonyl carbanion salts but also have a much higher configurational stability. Racemization of α-(*S*)-trifluoromethylsulfonyl and α-(*S*)-*tert*-butylsulfonyl carbanion salt follows first-order kinetics and is mainly an enthalpic process with small negative activation entropy. This is in accordance with a C_α–S bond rotation as rate-determining step. The C_α–S rotational barrier is mainly determined by steric effects and the n_C→σ*_{S–R} interaction, which is, according to NBO calculations, generally stronger in α-(*S*)-trifluoromethylsulfonyl carbanions than in α-(*S*)-alkylsulfonyl carbanions. In the crystal phase, the dimeric lithium α-(*S*)-trifluoromethylsulfonyl carbanion salts have similar O–Li contact ion-pair structures to the lithium α-(*S*)-*tert*-butylsulfonyl carbanions. They form in THF solution monomeric CIPs, which have one or two O–Li and most probably no C_α–Li bonds according to NMR spectroscopy. Ab initio calculations of the monomeric CIPs of methyl-substituted benzylic lithium α-(*S*)-*tert*-butylsulfonyl and α-(*S*)-trifluoromethylsulfonyl carbanion salts, which carry two ether molecules at the Li atom, gave different energy-minimum structures: an O,Li,O CIP for the α-(*S*)-trifluoromethylsulfonyl and an O,Li,C_α CIP for the α-(*S*)-*tert*-butylsulfonyl salt. Interestingly, the n_C→σ*_{S–CF₃} interaction is stronger in the O,Li,O CIP of the lithium α-(*S*)-trifluoromethylsulfonyl carbanion salt than in the free carbanion. In THF solution the Li atoms of the monomeric CIPs of α-(*S*)-trifluoromethylsulfonyl and α-(*S*)-*tert*-butylsulfonyl carbanion salts are expected to be coordinated by three instead of two THF molecules and thus adopt a CIP structure with only one O–Li bond. Like the corresponding α-(*S*)-phenylsulfonyl carbanions, alkyl-substituted benzylic α-trifluoromethyl- and α-(*S*)-*tert*-butylsulfonyl carbanions have planar anionic C atoms,

whereas those of the corresponding dialkyl-substituted carbanions are most likely slightly pyramidalized. The negative charge of the benzylic α -trifluoromethyl- and α -(*S*)-*tert*-butylsulfonyl carbanions interacts through conjugation with the phenyl group, which significantly contributes to the stabilization of the carbanions. According to NMR spectroscopy, the benzylic interaction is smaller in magnitude in α -trifluoromethyl- than α -(*S*)-*tert*-butylsulfonyl carbanions. These findings are supported by ab initio calculations and NBO analyses of counterion-free α -(*S*)-*tert*-butylsulfonyl and α -(*S*)-trifluoromethylsulfonyl carbanions, which showed the $n_{\text{C}} \rightarrow \sigma_{\text{S-CF}_3}^*$ and $\pi_{\text{C}_6\text{H}_5} \rightarrow \sigma_{\text{S-CF}_3}^*$ interactions to be more stabilizing than the $n_{\text{C}} \rightarrow \sigma_{\text{S-tBu}}^*$ interactions and the benzylic conjugation to be more important in the *tert*-butylsulfonyl than in the trifluoromethylsulfonyl carbanions. Furthermore, benzylic conjugation in the CIPs of the lithium salts is weaker than in the corresponding free carbanions according to the calculations. However, the main mode of the stabilization of α -(*S*)-trifluoromethylsulfonyl carbanions and α -sulfonyl carbanions in general is electrostatic interaction between the negative charge and the sulfonyl group.

Enantiomerically pure dialkyl-substituted lithium α -trifluoromethylsulfonyl carbanion salts are accessible through deprotonation of the corresponding chiral triflones with *n*BuLi, with an extrapolated half-life of racemization, for example, at -78°C of 30 d. The alkylation, acylation, and hydroxyalkylation of the chiral lithium α -trifluoromethylsulfonyl carbanion salts proceeded with high enantioselectivities to yield tertiary triflones. The attack of the electrophiles at the anionic C atom of the salts always occurred *anti* to the trifluoromethyl group. The overall two-step transformation of the dialkyl-substituted chiral triflone by means of the corresponding chiral carbanion and its reaction with an electrophile under formation of the tertiary triflone proceeds under retention of configuration.

The displacement of the sulfonyl group of a tertiary triflone by an ethyl group upon reaction with AlEt_3 gave the corresponding alkane with an all-carbon quaternary C atom with high enantioselectivity. Whether or not this alkylation of tertiary triflones is of general applicability remains to be demonstrated.

An efficient route to dialkyl-substituted chiral secondary triflones includes the following steps: 1) synthesis of chiral thiols from the corresponding chiral secondary alcohols, 2) the photochemical trifluoromethylation of the thiols with formation of the corresponding chiral trifluoromethylsulfanes, and 3) the racemization-free oxidation of the alkyl-substituted sulfanes by using common oxidizing reagents in the presence of a catalyst.

Experimental Section

All details of the synthesis and characterization of the sulfones and sulfonamides; kinetic measurements of α -sulfonyl carbanion salts and sulfonamides; and synthesis, characterization, and reactions of the α -sulfonyl carbanion salts are described in the Supporting Information.

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