Chiral Organometallic Reagents, XVI[1]

Enantiomerization of α-Thio-, α-Seleno-, and α-Telluro-Substituted Alkyllithium Compounds; Kinetic and Mechanistic Studies

Reinhard W. Hoffmann*, Ruprecht K. Dress, Thomas Ruhland, and Andreas Wenzel

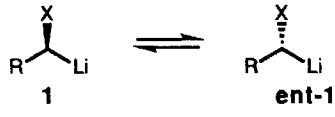
Fachbereich Chemie, Philipps-Universität,
D-35032 Marburg

Received April 18, 1995

Key Words: Enantiomerization / Organolithium compounds / Dynamic NMR spectroscopy

The rate of enantiomerization of the racemic α-phenylselenoalkyllithium compound **6** has been determined by dynamic NMR spectroscopy in [D_8]THF. The enantiomerization rate was found to be first order with respect to monomeric **6** and to show no conspicuous solvent dependence (diethyl ether; toluene + 1 eq. of THF) or change upon addition of $LiClO_4$. The marked steric effects on the enantiomerization rate found with the α-duryl- and α-mesityl-selenoalkyllithium compounds **7c** and **7d** suggest that rotation about the carbanion-selenium bond may be the rate-determining step in those sterically hindered systems. Similar steric effects were detected for the enantiomerization of the corresponding α-arylthio- and α-aryltelluroalkyllithium compounds **7j** and **7f**, but are absent with the α-arylsilyl-substituted alkyllithium compound **7o**. This finding, along with the fact that the phenyltelluro- (**7e**), phenylseleno- (**6**), and phenylthio-alkyllithium compounds (**7g**) have essentially the same enantiomerization barrier, lead us to propose that in these cases a reorganization within the contact ion pair is the rate limiting step for the enantiomerization.

α-Heterosubstituted alkyllithium compounds **1** are d^1 synthons[2] in organic synthesis, and since the entity **1** is chiral, these compounds are of interest as chiral building blocks for stereoselective synthesis.



1 **ent-1**

Accordingly, attention was focused on their configurational stability: Various studies showed that oxygen-[3,4] and amino-substituted[5] derivatives of **1** are configurationally stable on a macroscopic time scale, i.e. for ca. 10 min at −78 °C. On the other hand, sulfur-[6,7,8] and seleno-[9] substituted derivatives of **1** are configurationally labile on this time scale. However, fast (e.g. intramolecular) trapping reactions are sometimes faster than enantiomerization in such cases[6,10]. Such species may be called configurationally stable on a microscopic time scale. Our goal was therefore to increase the configurational stability of such organolithium compounds by some modification, which obviously would require knowledge of the enantiomerization mechanism. Calculations[11] and experiments[12] were carried out on the epimerization/enantiomerization of alkyllithium compounds, suggesting an associative process between two or more alkyllithium entitites. However, the enantiomerization of α-heterosubstituted alkyllithium compounds **1** may also be described by other mechanistic schemes. For this reason, the groups of H. J. Reich and ourselves initiated studies on the enantiomerization mechanism of alkyllithium compounds **1** with X = SR, SeR, and SiR_3. In this paper we detail our results.

Results and Discussion

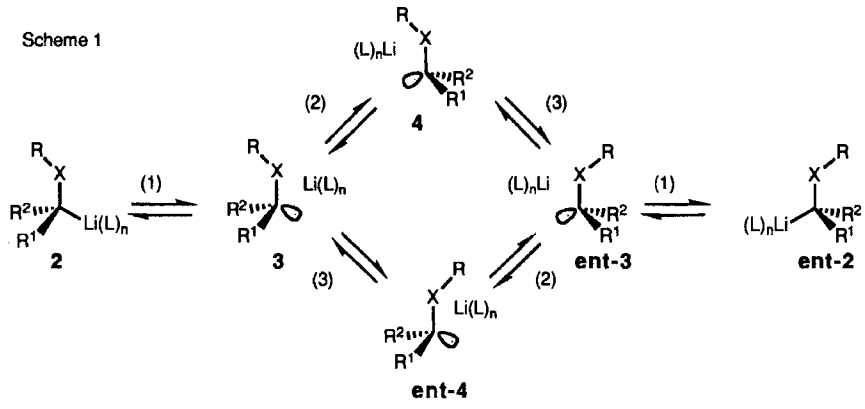
A limitation of all mechanistic studies is, that they rely on proposed reaction pathways, which can be disproven by experiments but not proven. A non-associative mechanism for the enantiomerization of **1** may involve the following steps:

The first step may be described as a decoordination of the carbanion from the lithium to form a contact ion pair. This would allow a relative motion of the anion and the cation within the ion pair. The second step could be the configurational inversion of the carbanion. Finally, a third step, rotation around the C^-−X bond, has to be added to complete the enantiomerization process. This is attributed to the fact that organolithium compounds **2** with X = S, Se, SiR_2 are stabilized by negative hyperconjugation[13], i.e. the carbanion lone pair and the X−R bond are arranged antiperiplanar[7] to allow maximum delocalization of the carbanion lone pair into the σ^*_{X-R}-orbital. Once inversion of **3** to **4** has occurred, the lone pair orbital in **4** is *syn*-periplanar to the X−R bond. Hence, a rotation step around the C^-−X-bond (step 3) is required to restore the negative hyperconjugation. Finally, coordination of the lithium cation to the carbanion would complete the enantiomerization scheme. Within the framework of this working hypothesis we tried to obtain clues by kinetic studies as to which of these steps would be the rate-limiting one for the total process.

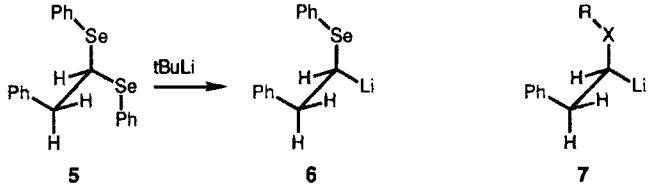
The system chosen for study was the α-phenylselenoalkyl-lithium compound **6**, because enantiomerization could be followed by coalescence of the ^{1}H-NMR signals of the diastereotopic protons in the benzyl moiety. The lithium

  0009−2940/95/0909−0861 $ 10.00+.25/0

Scheme 1



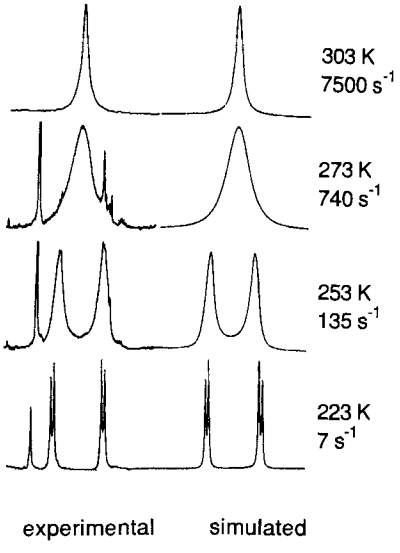
compound **6** was generated[14] by treatment of the selenoacetal **5** with freshly sublimed *tert*-butyllithium in THF.



Kinetic studies on the enantiomerization of **6** are meaningful only if the starting system is adequately defined, i.e. if the state of aggregation in the solvent to be used is known. Cryoscopic measurements in THF at −108 °C of a 0.15 M solution of **6** showed an aggregation of 1.04 ± 0.07[15]. Since aggregation increases with increasing temperature[16] and the kinetic measurements were to be run in the temperature range from −90 to 0 °C, we felt it necessary to ascertain the aggregation state of **6** at higher temperatures as well. For this purpose we used vapor-pressure osmometry, which could be carried out with THF solutions at 0 °C or with solutions in diethyl ether at ≥ −35 °C[17]. Due to the upper limit in the thermal stability of **6** (ca. −20 °C) the aggregation was determined at −35 °C in ether to be 1.0 ± 0.1. When **6** is monomeric in ether, it should also be monomeric at that temperature in the better dissociating solvent THF. Thus, we conclude that **6** is monomeric in THF in the temperature range from −100 to −35 °C. In addition information is needed on the nature of the ion pair structure of **6**. Coupling of a single ^{6}Li to the carbanion carbon is revealed by the NMR spectra with a ^{6}Li^{13}C coupling constant of 11 Hz, demonstrating that **6** is present in THF as a covalent species or at most as a contact ion pair. The C−H coupling constant of the anionic carbon is 119 Hz, showing that the anionic carbon in **6** is sp^3-hybridized, i.e. pyramidal.

The temperature dependence of the ^{1}H-NMR spectra of **6** was monitored in the temperature range from −90 to 0 °C. When the proton at the anionic carbon was decoupled, the benzylic protons appeared as a simple AB spin system at −50 °C, which coalesced on warming to 0 °C, becoming sharper on warming to 30 °C. The NMR lineshapes were simulated by using the program QUABEX[18].

Figure 1. Temperature dependence of the ^{1}H-NMR-line shapes of **6** in [D$_8$]THF



From an Eyring plot the activation parameters for the enantiomerization in THF were estimated to be $\Delta H^{\neq}$ = 11.7 ± 0.3 kcal mol^{-1} and $\Delta S^{\neq}$ = −2.9 ± 1.4 cal K^{-1} mol^{-1}. A decrease in the sample concentration from 0.3 mol l^{-1} to 0.1 mol l^{-1} did not lead to an alteration of the coalescence temperature. Enantiomerization of **6** is therefore a unimolecular process. Addition of up to 5 equivalents of $LiClO_4$ did not change the coalescence temperature significantly. Nevertheless intermolecular lithium/lithium exchange could be detected in a separate experiment with doubly labeled ^{13}C-^{6}Li-**6** on the basis of the coalescence of the C-Li coupling[19]. The coalescence temperature for the latter process rises from −98 °C in 0.29 M solution of **6** to −70 °C in 0.1 M solution (and up to −30 °C upon addition of 5 equivalents of PMDTA). The lithium/lithium exchange is therefore a process of higher order in the case of **6** and is unrelated to the unimolecular enantiomerization reported before.

In order to get some hint as to which step of Scheme 1 could be the rate-limiting one, we studied the solvent dependence of the enantiomerization rate of **6**. The data are summarized in the Table 1.

Table 1. Solvent dependence of the enantiomerization rate of **6**, activation parameters

Solvent	$\Delta G^{\ddagger}_{263}$ [a] (kcal mol^{-1})	$\Delta H^{\ddagger}$ [a] (kcal mol^{-1})	$\Delta S^{\ddagger}$ cal mol^{-1}K^{-1}
THF	12.5 ± 0.7	11.7 ± 0.3	-2.9 ± 1.4
Ether	12.6 ± 0.9	10.9 ± 0.6	-6.3 ± 1.5
Toluene + 3 equiv. of THF	11.9 ± 0.8	10.2 ± 0.6	-6.4 ± 1.6
Toluene + 2 equiv. of THF	11.8 ± 0.6	8.4 ± 0..	-12.8 ± 1.0
Toluene + 1 equiv. of THF	12.2 ± 1.2[b]		

[a] Statistical errors smaller than ±0.6 kcal mol^{-1} are not given as such. – [b] At the coalescence temperature of −10 °C.

The variations in ΔH^{+} are predominantly counterbalanced by changes in ΔS^{+}, so that the enantiomerization rate does not significantly vary with the solvent used. If the enantiomerization rate were defined by a conversion of **6** to the contact ion pair and on to a solvent-separated ion pair, a stronger solvent dependence and also a more negative activation entropy would be expected[20]. On the other hand, the absence of a solvent dependence of the enantiomerization rate did not give any clue as to which step in Scheme 1 is the rate-determining one. Could step (2) be the rate-determining one? Inversion barriers of α-thio-substituted carbanions were calculated by several groups[21,22]. The better the basis set of the calculations, the lower the activation barrier, falling as low as 0.5 kcal mol^{-1} for $CH_3S-CH_2^-$[22] or 1.1 kcal mol^{-1} for $CH_3S-CH^--CH_3$[23]. For this reason it is not very likely, that inversion constitutes the rate-limiting step in the enantiomerization of **6**. Nevertheless, inversion, if it were rate-determining, could probably be detected by a sizeable kinetic α-deuterium isotope effect. The related process, inversion at the nitrogen atom of dimethylamine is subject to an isotope effect $k_H/k_D = 24$, indicating a tunnel effect[24]. For this reason we determined the enantiomerization rate for α-D-**6**. The coalescence phenomena in the ^{1}H-NMR spectra of α-D-**6** were indistinguishable from those in α-H-**6**. The kinetic isotope effect could therefore not exceed the limits $0.87 < k_H/k_D < 1.3$. If there is an isotope effect on the enantiomerization of **6**, it is so small that it would be inconsistent with step (2) in Scheme 1 being the rate determining step for the enantiomerization.

Could the third step, rotation around the $C^- - XR$ bond in **6**, be the rate-limiting one?[25] Rotation is the rate-limiting step for enantiomerization of α-phenylsulfonyl-alkyllithium and other alkylsulfonyl-alkyllithium compounds[26]. Likewise, significant rotational barriers have been reported for diphenylphosphinomethyllithium[27] and bis-phenylthio-(phenyldimethylsilyl)methyllithium[28]. The rotation process implies that groups within a molecule have to be moved past one another. Processes of this sort are amenable to steric hindrance. For this reason we studied the effects caused by increasing the size of the aryl group in **6**. Several aryl-seleno-alkyllithium compounds **7** were generated from the corresponding selenoacetals and the enantiomerization barriers were estimated from the coalescence temperature of the benzylic proton signals in the ^{1}H-NMR spectra. The results are compiled in Table 2.

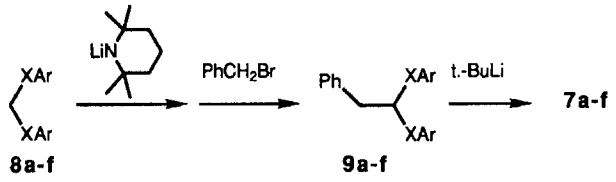
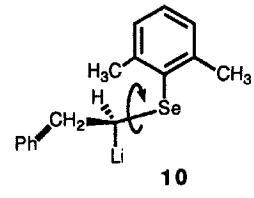


Table 2. Substituent effects on the enantiomerization barrier of **7** (X = Se) derived from the coalescence temperature of the benzylic protons in the ^{1}H-NMR spectra

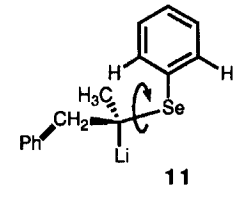
	R	T_c (°C)	$\Delta\nu$ (Hz) / T (°C)	$\Delta G^{\ddagger}$ (kcal mol^{-1})
6	Phenyl	0	248 / -40	12.4
7a	o-Tolyl	5	269 / -50	12.7
7b	p-Tolyl	-5	230 / -50	12.3
7c	Mesityl	>0	56 / -60	> 14.3
7d	Duryl	>20	35 / -60	> 14.5

Duryl = 2,3,5,6-tetramethylphenyl; Mesityl = 2,4,6-trimethylphenyl.

It is obvious, that an *o*-tolyl or a *p*-tolyl residue on selenium does not effect the enantiomerization rate. Two *ortho*-positioned methyl groups, however, increase the enantiomerization barrier to the point, that no coalescence, not even line broadening of the signals of the diastereotopic benzylic hydrogen atoms could be observed within the accessible temperature range (i.e. <0 °C). Thus, only a lower limit to the enantiomerization barrier can be given. This is the manifestation of a substantial steric effect on the enantiomerization process. This effect becomes understandable, if a rotation of the aryl group past the hydrogen atom at the carbanion center is to be effected (cf. **10**).



10

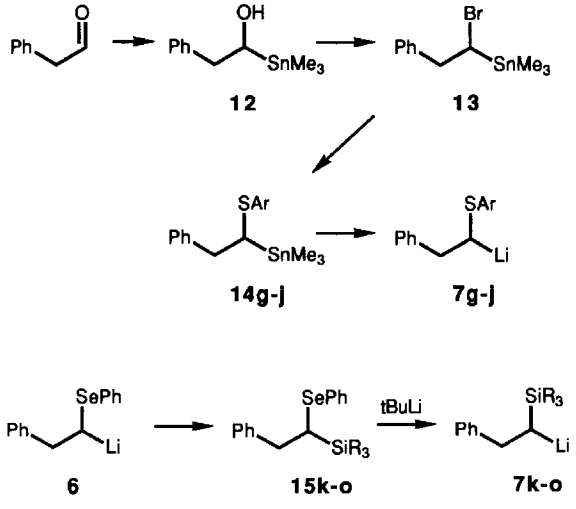


11

With two *ortho*-methyl groups, one cannot avoid moving one of them past the hydrogen atom indicated in **10**. If such steric hindrance to rotation is the reason for slowing down the enantiomerization of **7c** or **7d**, steric hindrance should be the same, when the position of the hydrogen atom and of the methyl group are interchanged. For this reason we generated the lithium compound **11** and, likewise, could not observe coalescence of the signals of the benzylic hydrogen atoms; $\Delta G^{\ddagger}_{253}$ for the enantiomerization of **11** must be >12.9 kcal mol^{-1}. Thus, at least in the cases of **7c**, **7d**, and

11 rotation around the C$^-$–SeAr-bond is rate-limiting for the enantiomerization. The extent of the underlying steric hindrance should depend on the length of the carbanion–heteroatom bond. With other heteroatoms at the carbanionic site it should be different.

For this reason we measured the enantiomerization rates for a series of tellurium- and sulfur-substituted analogs of **6**. The lithium compounds **7e** and **7f** were generated from the telluroacetals **9e** and **9f**. The lithium compounds **7g–o** and their precursors were prepared according to the following scheme:

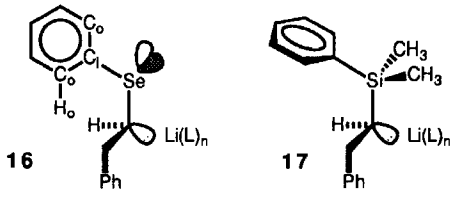


For the definition of Ar or R in **g-o**, cf. Table 3

The activation parameters for the enantiomerization of these derivatives of **7** in [D$_8$]THF are recorded in Table 3.

The activation entropies are usually negative and of small magnitude. The reported variations may not be significant in view of the usual uncertainties in deriving activation entropies from rate data. Likewise, the activation enthalpies for the sulfur, selenium, and tellurium cases do not vary much, unless mesityl or duryl substituents are involved. Probably the most reliable picture can be gained from the free energies of activation, which are reasonably constant including also the silicon-substituted cases **7k–7o** to be discussed later.

The situation with the tellurium compounds **7e** and **7f** is straightforward: the phenyltellurium compound **7e** shows an enantiomerization barrier very similar to that of **6**, the duryltellurium compound **7f** shows the effects of (some) steric hindrance on the enantiomerization process, the barrier being increased by 2.5 kcal mol^{-1} relative to that of **7e**. When the steric hindrance caused by a duryl substituent increases the barrier to rotation about the "long" carbon–tellurium bond by 2.5 kcal mol^{-1} the effect should be >2.5 kcal mol^{-1} about the "shorter" carbon–selenium bond, and even larger about the even shorter carbon–sulfur bond. This prediction is in qualitative accord with the results reported. The unexpected result was, that no steric effects were observed in the enantiomerization of the mesityldimethyl*silyl* derivative **7o** compared to the phenyldimethylsilyl derivative **7l**. This offered in fact the opportunity to gain a deeper understanding of the factors controlling the rotation around the carbanion-heteroatom bond:



In the ground state of **6** (cf. **16**), the carbon–lithium and selenium–phenyl bonds are antiperiplanar[7] to allow stabilization of the negative charge by hyperconjugation[13]. This places the carbanion lone pair gauche with respect to the two nonbonding heteroatom lone pairs, a situation which should destabilize the system. This destabilization could be decreased by delocalization of the lone pairs from the heteroatom into the π*-orbital of the aryl group. This causes the aryl group to lie with all its carbon atoms in the plane

Table 3. Enantiomerization barriers[a] for the α-hetero-substituted alkyllithium compounds **7e–7o** in [D$_8$]THF

7	Heteroatom X	R	$\Delta G^{\ddagger}_{263}$ (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1}K^{-})
e	Te	Phenyl	11.8 ± 0.6	10.0 ± 0.6	-6.8 ± 1.1
f	Te	Duryl	13.9 ± 0.8	14.7 ± 0.6	3.0 ± 1.5
g	S	Phenyl	11.3 ± 0.6	10.6 ± 0.6	-2.7 ± 0.1
h	S	3-CF_3-C_6H_4-	11.4 ± 2	9.3 ± 1	-8 ± 4
i	S	4-CH_3O-C_6H_4-	11.4 ± 0.6	10.2 ± 0.6	-4.5 ± 1
j	S	Duryl	> 13.9		
k	$SiMe_2$	Methyl	12.6 ± 1	11.3 ± 0.6	-5 ± 2
l	$SiMe_2$	Phenyl	11.8 ± 0.8	12.4 ± 0.6	+2 ± 1.4
m	SiPhMe	Phenyl	11.7 ± 0.6	9.7 ± 0.6	-7.9 ± 1
n	$SiPh_2$	Phenyl	11.9 ± 0.6	7.0 ± 0.6	-18.4 ± 1.1
o	$SiMe_2$	Mesityl	11.8 ± 1.3	11.1 ± 0.6	-2.6 ± 2.5

[a] Statistical errors smaller than ±0.6 kcal mol^{-1} were not given as such.

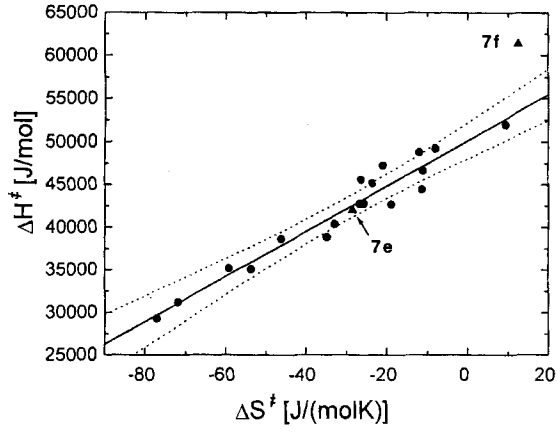
of the lithium-carbanion-selenium entity. This enforced conformation around the C_{ipso}–selenium (heteroatom) bond is just the one found in the crystal structures of phenylthiomethyllithium[29] or diphenylphosphinomethyllithium[27]. When rotation around the carbanion–selenium bond commences, the carbanion lone pair has to rotate past the heteroatom lone pairs. In this situation delocalization of the lone pairs into the aryl ring becomes even more mandatory. Therefore, during the whole rotation process, the aryl ring maintains this orientation, i.e. the atoms C_o–C_i–Se–C_{anion} remain coplanar possibly even when H_o passes by the hydrogen at the carbanion center. This results in a substantial steric effect of the *ortho*-disubstituted aryl groups, which behave like a large propeller blade. This should hold for the tellurium and sulfur cases as well, but not for silicon because the lithium compound **7l** does not have lone pairs on the heteroatom, which would suffer destabilizing interactions with the carbanion lone pair and which would have to be delocalized into the aryl group. Hence, there is no reason for any preferred conformation around the C_i-silicon bond in **7l–o**. The aryl group can make itself "flat" during rotation around the carbanion–silicon bond (cf. **17**) and hence a phenyl and a mesityl group or methyl groups on silicon (cf. **7k**) make no difference as seen from Table 3.

Induced by these considerations we studied, whether the energy level of the π^* orbitals of an aryl group exerts any influence on the enantiomerization barrier of arylthioalkyllithium compounds. The data in Table 3 show that a donor substituted aryl ring (**7i**) and an acceptor-substituted aryl ring (**7h**) do not lead to altered enantiomerization rates. Any such effect must be smaller than the inaccuracies of the rate measurements used.

At this stage it is clear, that inversion [step (2) in Scheme 1] is not the rate-determining step in the enantiomerization of the compounds **6** and **7** investigated, and that rotation around the carbanion–heteroatom bond [step (3) Scheme 1] is rate-determining for the enantiomerization of the durylTelluro-, durylseleno-, and durylthio compounds. This leaves it open, whether rotation [step (3)] or motion within the ion pair [step (1) in Scheme 1] is the rate-determining step in the other cases. At this moment indirect arguments favor the latter alternative: If rotation were the rate-determining step in these cases as well, one would expect the enantiomerization barrier to rise in the series PhTe < PhSe < PhS as has been found for the duryl-substituted tellurium and selenium derivatives **7d** and **7f**, according to an increase in the steric hindrance with a shorter carbanion-heteroatom bond. The data in Table 3 do not bear out this point. The silicon-substituted cases constitute a different series, as far as rotation about the carbanion–heteroatom bond is concerned. Here, at every 60° rotation one silicon–R bond is in a favorable position to stabilize the carbanion by negative hyperconjugation. There may be a difference between a methyl and an aryl group on silicon in this respect. But such differences are not reflected in the enantiomerization barriers found for **7k–7o**. If rotation were rate-determining for all the sulfur and selenium compounds but not for the silicon ones, these would constitute two different families, regarding the rate-determining step of the enantiomerization.

In fact, the enantiomerization of the tellurium compound **7f** constitutes the only example, in which rotation is rate-determining *and* for which activation barriers could be determined. So the question could be asked, whether the other cases studied are similar to **7f** or to the silicon series **7k–o**. This cannot be rigorously answered but some hints could come from a $\Delta H^{\neq}/\Delta S^{\neq}$ correlation[30], in which reactions passing through the same type of rate-determining transition state could fall on one correlation line. We therefore plotted $\Delta H^{\neq}$ against $\Delta S^{\neq}$ for our data (Figure 2)[31].

Figure 2. $\Delta H^{\neq}/\Delta S^{\neq}$-Correlation for the racemization of the α-substituted alkyllithium compounds **7**



The majority of the data are in accordance with a correlation, which includes the silicon-substituted cases and which excludes the durylTellurium case **7f**. Thus, based on these arguments we suggest, that in all enantiomerization processes, studied here, except for the duryl- and mesityl-substituted tellurium, selenium, and sulfur compounds the rate-determing step is the first one in Scheme 1, the decoordination of the lithium cation from the carbanion and a motion within the contact ion pair.

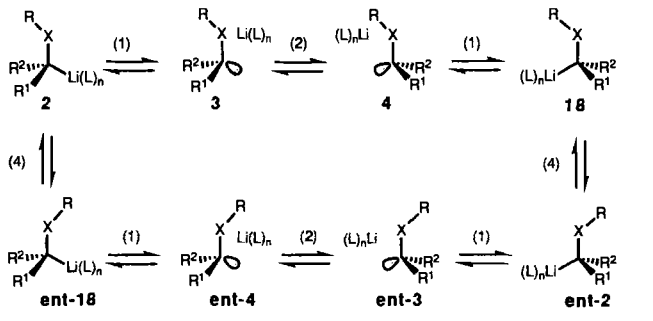
This leaves us without any information on the height of the rotational barrier [i.e. step (3) in Scheme 1] in those cases. Ab initio calculations on the MP2/6-31+G* level for $CH_3SCH_2^-$[22] resulted in a rotational barrier of 12.5 kcal mol^{-1} (less elaborate basis sets resulted in lower barriers) and for CH_3SCH^--CH_3 of 10.9 kcal mol^{-1}[23]. Stronger negative hyperconjugation, as would prevail in C_6H_5S-CH^-–R as a consequence of the *sp^2-carbon*–sulfur bond, should lead to an increased rotational barrier. However, weakened negative hyperconjugation, which could result from the coordination of the lithium cation to the carbanion in the contact ion pair should lead to a lower barrier of rotation[28]. All in all, the rotational barrier could be as high as but also lower than the enantiomerization barrier observed for **7g** of 11.3 kcal mol^{-1}.

The calculations performed[23] on CH_3S–CH^-CH_3 addressed yet another point, whether rotation [step (3) in Scheme 1] and inversion [step (2) in Scheme 1] proceed in

a concerted manner. Combined rotation and inversion pass through stationary states with two imaginary frequencies, which lie at least 18 kcal mol^{-1} above the ground state[23]. Thus, rotation and inversion of α-thio-substituted ethanides are no concerted processes but separate transformations.

With all this information we have gained a much more precise picture of the enantiomerization of α-thioalkyllithium and related compounds, a picture which is in accordance with our working hypothesis (cf. Scheme 1). The results of H. J. Reich[28] however, led us to modify the hypothesis regarding one aspect: Rotation around the carbon–sulfur bond should be more facile when the lithium is attached to the carbanion[28] as in **18** [cf. step (4) Scheme 2] than in the free carbanion. Therefore, Scheme 2 is a better description of the enantiomerization scenario.

Scheme 2



(1): Motion within the contact ion pair. - (2) Inversion. - (4) Rotation in the organolithium compound.

We assume that intra-ion-pair motion [step (1)] will be the highest barrier, unless excessive steric hindrance raises the rotational barrier. The scheme, of course, may find future modification. It is in a way unsatisfactory, that the methods available today are not refined enough to reveal further details of the enantiomerization that happens in the contact ion pair. On the other hand, we attained one of our goals, we discovered a modification of the α-aryltelluro-, α-arylseleno-, or α-arylthio-substituted alkyllithium compounds that leads to increased configurational stability, vic. the attachment of the duryl or mesityl residues to the heteroatom. We are at present exploiting this finding in stereoselective synthesis.

Essential financial support of this work described came from the *Deutsche Forschungsgemeinschaft* (SFB 260) and the *Graduierten-Kolleg "Metallorganische Chemie"* which provided a fellowship to T. R. and K. R. D. We would like to thank these institutions as well as the *Fonds der Chemischen Industrie* and the *Studienstiftung des Deutschen Volkes* for their support.

Experimental

All temperatures quoted are uncorrected. – All experiments with organolithium compounds were carried out in dried glassware under nitrogen or argon. – ^1H NMR, ^{13}C NMR, Bruker AC-300, AM-400, AMX-500. – Boiling range of petroleum ether: 40–60°C. – Flash chromatography: Silica gel Si 60, E. Merck AG, Darmstadt, 40–63 μm.

1. *2-Phenyl-1,1-bis(phenylseleno)ethane* (**5**)[32]: To a suspension of 3.4 g (25 mmol) of zinc chloride in 40 ml of CH_2Cl_2 was added under nitrogen 15.9 g (0.1 mol) of selenophenol. After cooling to 0°C 6.1 g (50 mmol) of freshly distilled phenylacetaldehyde was added over 30 min. After stirring of the mixture for 3 h it was allowed to reach room temperature. After 12 h 200 ml of petroleum ether was added. The phases were separated and the organic phase was washed twice with 75 ml of aqueous 7% KOH each, twice with 75 ml of water each, and once with 50 ml of brine. The organic phase was dried with K_2CO_3 and concentrated. The residue was purified by flash chromatography over silica gel with petroleum ether/chloroform (10:1) to give 17.3 g (82%) of **5** as a viscous oil. – ^1H NMR (300 MHz, $CDCl_3$): δ = 3.19 (d, *J* = 7.2 Hz, 2H), 4.55 (t, *J* = 7.2 Hz, 1H), 7.19–7.47 (m, 15H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.5, 44.1, 126.8, 128.0, 128.3, 129.0, 129.2, 130.4, 134.7, 139.0. – $C_{20}H_{18}Se_2$ (416.3): calcd. C 57.71, H 4.36; found C 57.70, H 4.38.

1-Deuterio-2-phenyl-1,1-bis(phenylseleno)ethane (α-D-**5**): To a solution of 0.20 g (2.0 mmol) of diisopropylamine and 2.30 g (2.04 mmol) of potassium *tert*-butoxide in 5 ml of THF was added at –78°C 1.2 ml (1.6 mmol) of a 1.3 M solution of *n*-butyllithium in hexane. After stirring for 10 min a solution of 0.50 g (1.2 mmol) of **5** in 2 ml of THF was added. After further stirring for 3 min a solution of 0.5 ml (0.1 mol) of CD_3OD in 3 ml of THF was added at –78°C. The mixture was allowed to reach room temp., diluted with 40 ml of petroleum ether and washed twice with 20 ml of 7% aqueous KOH each and once with 10 ml of brine. The organic phase was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography with petroleum ether/chloroform (10:1) to give 0.45 g (90%) of **5** which was monodeuterated at C_α in 90% yield. This material was again subjected to the same procedure to give 0.40 g (80%) of completely α-deuterated **5**.

[1-^{13}C]-2-Phenyl-1,1-bis(phenylseleno)ethane (1-^{13}C-**5**): A solution of 26.5 mmol of benzylmagnesium chloride in ether was frozen in liquid nitrogen and the flask was evacuated. It was connected to a balloon filled with carbon dioxide liberated from 2.50 g (12.7 mmol) of ^{13}C-barium carbonate. The carbon dioxide was allowed to enter the flask which was removed from the liquid nitrogen bath. The content was vigorously stirred for 2 h after which time 50 ml of 15% aqueous HCl was added. The phases were separated and the aqueous phase was extracted eight times with 50 ml of ether each. The combined organic phases were dried with $MgSO_4$ and concentrated. The crude phenylacetic acid was recrystallized from 5 ml of petroleum ether to give 1.21 g (70%) of a colorless solid, m.p. 77°C.

This solid was dissolved in 10 ml of THF. 2.0 ml (20 mmol) of 10 M $BH_3 \cdot SMe_2$ was added to the solution at 0°C over 10 min. After reaching room temp. the mixture was stirred for 1 h and then hydrolyzed slowly with 5 ml of a THF/water mixture (1:1). When the hydrogen evolution had ceased 2 g (14 mmol) of potassium carbonate was added, the phases were separated and the aqueous phase was extracted with 20 ml of ether. The combined organic phases were washed twice with 10 ml of aqueous 7% KOH each and once with 10 ml of brine. The solvents were removed in vacuo 10 ml of methanol was added to the residue and the methanol was removed by distillation. This procedure was repeated three times to leave 1.12 g of a residue, which was purified by flash chromatography with ether to give 0.97 g (89%) of 1-^{13}C-2-phenylethanol as a colorless liquid.

The alcohol was dissolved in 30 ml of CH_2Cl_2, 70 ml of a 5% aqueous $NaHCO_3$ solution and then 1.5 mg (10 μmol) of 2,2,6,6-tetramethylpiperidine oxide were added at 0°C to the solution. Over 2 min 1.4 g (9.8 mmol) of calcium hypochlorite was added with stirring to the mixture in small portions. After 8 min the mixture was filtered, and the filter residue was extracted three times

with 30 ml of CH_2Cl_2 each. The combined organic phases were washed with 20 ml of a 5% aqueous $NaHSO_4$ solution and 20 ml of brine, then dried with Na_2SO_4 and concentrated. The resulting 1-^{13}C-2-phenylacetaldehyde was immediately converted into the selenoacetal as described above to give 1.94 g (58%) of 1-^{13}C-**5**.

2. *Bis(o-tolylseleno)methane* (**8a**): To a solution of 2.8 g (16 mmol) of 2-bromotoluene in 25 ml of THF was slowly added at −78 °C 35 mmol of a solution of *tert*-butyllithium in hexane. After stirring for 1 h at this temperature the mixture was allowed to reach 0 °C. Then 1.3 g (16 mmol) of selenium powder was added in small portions resulting in a clear faintly yellow solution. After stirring for 30 min at room temp., a solution of 0.66 ml (8.2 mmol) of diiodomethane in 2 ml of THF was added. After stirring for 12 h 2 ml of water and 150 ml of diethyl ether were added. The organic phase was washed twice with 50 ml of water each and once with 50 ml of brine, dried with $MgSO_4$ and concentrated. Flash chromatography of the residue with petroleum ether furnished 2.3 g (79%) of **8a** as a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.46 (s, 6H), 4.23 (d, $J_{H,Se}$ = 12 Hz, 2H), 7.19−7.25 (several m, 6H), 7.57 (dd, J = 7.4 and 1.5 Hz, 2H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5, 22.2, 126.6, 127.4, 130.0, 132.0, 132.1, 139.4. − $C_{15}H_{16}Se_2$ (354.2): calcd. C 50.86, H 4.55; found C 50.87, H 4.55.

3. *Bis(p-tolylseleno)methane* (**8b**): To a solution of 2.4 g (14 mmol) of *p*-selenocresol in 20 ml of anhydrous ethanol was added 530 mg (14 mmol) of sodium borohydride in small portions at 0 °C. When the vigorous hydrogen evolution had ceased the mixture was stirred for 30 min at room temp. A solution of 0.60 ml (7.4 mmol) of diiodomethane in 3 ml of ethanol was added. After stirring for 12 h the mixture was worked up as described under 2. to give 1.9 g (77%) of **8b** as a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 6H), 4.16 (d, $J_{H,Se}$ = 12 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 21.8, 127.1, 129.9, 130.4, 137.6. − $C_{15}H_{16}Se_2$ (354.2): calcd. C 50.86, H 4.55; found C 50.84, H 4.44.

4. *Bis(2,4,6-trimethylphenylseleno)methane* (**8c**): 4.0 g (20 mmol) of 2,4,6-trimethylselenophenol, 760 mg (20.1 mmol) of sodium borohydride, and 1.0 ml (12 mmol) of diiodomethane were allowed to react as described under 3. The crude product was recrystallized from ethanol to give 2.6 g (63%) of **8c** as light-sensitive needles, m.p. 46 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 6H), 2.45 (s, 12H), 3.73 (d, $J_{H,Se}$ = 10 Hz, 2H), 6.90 (s, 3H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3, 20.9, 24.3, 128.5, 129.1, 138.5, 143.0. − $C_{19}H_{24}Se_2$ (410.3): calcd. C 55.62, H 5.89; found C 55.48, H 5.83.

5. *Bis(2,3,5,6-tetramethylphenylseleno)methane* (**8d**): The material was prepared from 6.40 g (30 mmol) of 1-bromo-2,3,5,6-tetramethylbenzene as described under 2. Colorless plates from diethyl ether, m.p. 104−106 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (s, 12H), 2.43 (s, 12H), 3.75 (d, $J_{H,Se}$ = 11 Hz, 2H), 6.92 (s, 2H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.06, 21.13, 21.4, 132.2, 134.0, 138.4. − $C_{21}H_{28}Se_2$ (438.4): calcd. C 57.54, H 6.44; found C 57.71, H 6.68.

6. *Bis(phenyltelluro)methane* (**8e**)[33]: 6.67 ml (42.5 mmol) of bromobenzene, 85.0 mmol of *tert*-butyllithium in hexane, 5.42 g (42.5 mmol) of tellurium powder, and 1.71 ml (21.2 mmol) of diiodomethane were allowed to react as described under 2. The crude product had to be purified immediately by chromatography over alumina (neutral, activity II) with petroleum ether/ether (10:1) to give 6.2 g (69%) of **8e** as a light-sensitive dark orange oil. On standing in the refrigerator the material crystallized, m.p. 33−36 °C, ref.[33] 35−36 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s + d, $J_{H,Te}$ = 18.9 Hz, 2H), 7.14−7.34 (m, 6H), 7.68−7.89 (m, 4H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −36.8 (s + d, $J_{C,Te}$ = 215 Hz), 115.9, 127.9, 129.2, 137.0. − $C_{13}H_{12}Te_2$ (423.4): calcd. C 36.88, H 2.86; found C 36.77, H 2.89.

7. *Bis(2,3,5,6-tetramethylphenyltelluro)methane* (**8f**): From 3.51 g (16.5 mmol) of 1-bromo-2,3,5,6-tetramethylbenzene as described under 6.: 3.1 g (70%) as a brown solid, m.p. 104 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 12H), 2.55 (s, 12H), 3.57 (s + d, $J_{H,Te}$ = 18.5 Hz, 2H), 6.95 (s, 2H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −36.7, 21.6, 26.6, 127.3, 132.7, 133.3, 140.3. − $C_{21}H_{28}Te_2$ (535.7): calcd. C 47.09, H 5.27; found C 47.21, H 5.43.

8. *2-Phenyl-1,1-bis(o-tolylseleno)ethane* (**9a**): 7.6 mmol of *n*-butyllithum in hexane was slowly added at −78 °C to a solution of 1.30 ml (7.8 mmol) of 2,2,6,6-tetramethylpiperidine in 30 ml of THF. After stirring for 15 min a solution of 2.30 g (6.5 mmol) of **8a** in 10 ml of THF was added. After the mixture had been stirred for 1 h at −78 °C a solution of 2.3 ml (19.3 mmol) of benzyl bromide in 3 ml of THF was added. After further stirring for 2 h at −78 °C the mixture was allowed to reach room temp. 2 ml of water and 100 ml of ether were added.The organic phase was washed twice with 50 ml of water each and once with 50 ml of brine, dried with $MgSO_4$ and concentrated. Flash chromatography of the residue with petroleum ether furnished 2.1 g (73%) of **9a** as a slightly yellowish oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (s, 6H), 3.32 (d, J = 7.5 Hz, 2H), 4.02 (t, J = 7.5 Hz, 1H), 7.10−7.40 (several m, 13H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 43.4, 44.0, 126.7, 127.3, 127.5, 128.5, 129.7, 130.5, 132.1, 132.3, 138.7, 139.8. − $C_{22}H_{22}Se_2$ (444.3): calcd. C 59.47, H 4.99; found C 59.65, H 5.00.

9. *2-Phenyl-1,1-bis(p-tolylseleno)ethane* (**9b**): From 1.3 g (3.7 mmol) of **8b** as described under 8.; 1.2 g (73%) of a colorless solid, m.p. 48−51 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 6H), 3.11 (d, J = 7.6 Hz, 2H), 4.25 (t, J = 7.5 Hz, 1H), 7.00−7.35 (several m, 13H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 43.7, 44.2, 126.7, 127.2, 128.0, 128.2, 129.8, 130.3, 137.7, 130.4. − $C_{22}H_{22}Se_2$ (444.3): calcd. C 59.47, H 4.99; found C 59.41, H 5.02.

10. *2-Phenyl-1,1-bis(2,4,6-trimethylphenylseleno)ethane* (**9c**): From 2.30 g (5.6 mmol) of **8c** as described under 8.; 2.3 g (82%) of a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 6H), 2.34 (s, 12H), 3.09 (d, J = 7.3 Hz, 2H), 4.22 (t, J = 7.3 Hz, 1H), 6.88 (s, 4H), 7.03 (broad d, 2H), 7.21 (m, 3H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 24.3, 43.2, 44.4, 126.5, 128.1, 128.5, 129.0, 138.5, 139.6, 141.2. − $C_{26}H_{30}Se_2$ (498.4): calcd. C 62.25, H 6.07; found C 62.58, H 6.11.

11. *2-Phenyl-1,1-bis(2,3,5,6-tetramethylphenylseleno)ethane* (**9d**): From 2.0 g (4.6 mmol) of **8d** as described under 8.; 1.3 g (53%) of colorless needles from ether, m.p. 92−96 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 12H), 2.32 (s, 12H), 3.10 (d, J = 7.3 Hz, 2H), 4.21 (t, J = 7.3 Hz, 1H), 6.90 (s, 2H), 7.02 (m, 2H), 7.20 (m, 3H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.06, 21.12, 44.1, 44.2, 126.5, 128.0, 128.9, 132.2, 133.8, 133.9, 138.7, 139.6. − $C_{28}H_{34}Se_2$ (528.5): calcd. C 63.63, H 6.48; found C 63.43, H 6.46.

12. *2-Phenyl-1,1-bis(phenyltelluro)ethane* (**9e**)[33]: From 1.00 g (2.3 mmol) of **8e** as described under 8. All operations including chromatography over alumina (neutral, activity II) with petroleum ether/ether (8:1) had to be performed rapidly with complete exclusion of light to give 0.65 g (53%) of **9e** as a dark orange oil. The material crystallized on standing in the refrigerator, melting range 43−51 °C, ref.[33]: 38.5−39.5 °C. − ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 3.41 (d, J = 7.5 Hz, 2H), 4.93 (t, J = 7.5 Hz, 1H), 6.9−7.1 (several m, 11H), 7.74 (dd, J = 7.4 and 1.5 Hz, 4H). − ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = −4.3, 46.8, 117.0, 126.8, 128.4, 128.5, 129.3, 129.4, 140.1, 141.7. − $C_{20}H_{28}Te_2$ (513.6): calcd. C 46.78, H 3.53; found C 46.73, H 3.53.

13. *2-Phenyl-1,1-bis(2,3,5,6-tetramethylphenyltelluro)ethane* (**9f**): From 280 mg (0.52 mmol) of **8f** as described under 8. The reaction mixture was allowed to reach room temp. over 1 h. All the solvents were immediately removed i.vac. and the residue was extracted five times with 20 ml of boiling petroleum ether each. The combined extracts were immediately concentrated to give a dark yellow viscous oil which was immediately purified by chromatography over alumina (neutral, activity II) with petroleum ether/ether (8:1) to give 210 mg (65%) as a brown viscous oil. The material solidified upon standing in the refrigerator, m.p. 89–91 °C. – ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 2.12 (s, 12H), 2.60 (s, 12H), 3.44 (d, *J* = 7.7 Hz, 2H), 4.77 (t, *J* = 7.7 Hz, 1H), 6.80 (s, 2H), 6.99 (m, 5H). – ^{13}C NMR (75 MHz, [D$_6$]benzene): δ = –4.1, 21.7, 27.2, 47.9, 126.7, 128.6, 128.7, 133.2, 133.4, 140.9, 142.2. – $C_{28}H_{34}Te_2$ (625.8): calcd. C 53.74, H 5.48; found C 53.85, H 5.53.

14. *1-Phenyl-2,2-bis(phenylseleno)propane:* 0.98 g (7.3 mmol) of 1-phenylacetone, 2.30 g (14.6 mmol) of selenophenol and 0.50 g (3.7 mmol) of zinc chloride were allowed to react as described under 1. Flash chromatography with petroleum ether/ether (98:2) furnished 2.24 g (71%) of the product as a colorless solid, m.p. 103 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 3H), 3.24 (s, 2H), 7.18–7.31 (m, 11H), 7.56–7.60 (m, 4H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7, 47.7, 52.9, 126.7, 127.6, 128.5, 128.7, 130.9, 136.8, 137.7, 140.0. – $C_{21}H_{20}Se_2$ (430.3): calcd. C 58.62, H 4.68; found C 58.78, H 4.61.

15. *1-Bromo-2-phenyl-1-trimethylstannylethane* (**13**): A solution of lithium diisopropylamide was prepared from 120 ml of THF, 6.6 g (65.3 mmol) of diisopropylamine and 51 ml (66 mmol) of a 1.28 M solution of *n*-butyllithium in hexane. To this solution were added at –78 °C 10.0 g (60.7 mmol) of trimethyltin hydride and after stirring for 20 min a solution of 7.3 g (61 mmol) of phenylacetaldehyde in 20 ml of THF. The mixture was allowed to reach room temp., 300 ml of petroleum ether was added. The organic phase was washed twice with 100 ml of water each, once with 100 ml of brine, dried with Na_2SO_4 and concentrated i.vac. The residue was immediately added to a precooled (0 °C) solution of 15.8 g (60.3 mmol) of triphenylphosphane and 20.0 g (60.3 mmol) of tetrabromomethane in 30 ml of CH_2Cl_2. After stirring of the mixture at 0 °C for 3 h and at room temp. for 12 h the solvents were removed i.vac. and the residue was extracted ten times with 100 ml of petroleum ether each at reflux. The combined extracts were concentrated and the residue was chromatographed over silica gel with petroleum ether to give 15.1 g (72%) of **13** as a colorless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 3.19 (dd, *J* = 13.8 and 8.7 Hz, 1H), 3.36 (dd, *J* = 13.8 and 8.7 Hz, 1H), 3.72 (t, *J* = 8.7 Hz, 1H), 7.13–7.26 (m, 5H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = –9.5, 37.8, 43.8, 126.9, 128.5, 128.8, 140.1. – $C_{11}H_{17}BrSn$ (347.9): calcd. C 37.94, H 4.92; found C 37.99, H 4.84.

16. *2-Phenyl-1-phenylthio-1-trimethylstannylethane* (**14g**): To a solution of 0.49 g (4.5 mmol) of thiophenol and 0.17 g (3.0 mmol) of KOH in 30 ml of methanol was added under nitrogen 0.51 g (1.5 mmol) of **13**. The mixture was kept at reflux for 3 h. After cooling 100 ml of petroleum ether was added. The mixture was washed three times with 30 ml of 7% aqueous KOH each, 30 ml of water, and once with 20 ml of brine. The combined organic phases were dried with $MgSO_4$ and concentrated. Flash chromatography of the residue with petroleum ether furnished 0.44 g (79%) of **14g** as a colorless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 9H), 2.88 (dd, *J* = 10.0 and 13.7 Hz, 1H), 3.18 (dd, *J* = 5.0 and 10.0 Hz, 1H), 3.29 (dd, *J* = 5.0 and 13.7 Hz, 1H), 7.15–7.41 (m, 10H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = –9.4, 30.4, 39.9, 125.8, 126.5, 128.4, 128.8, 129.0, 141.1. – $C_{17}H_{22}SSn$ (377.1): calcd. C 54.14, H 5.88; found C 54.38, H 5.88.

17. *2-Phenyl-1-(3-trifluoromethylphenylthio)-1-trimethylstannylethane* (**14h**): 0.52 g (1.5 mmol) of **13** and 0.80 g (4.5 mmol) of 3-(trifluoromethyl)thiophenol[34] were allowed to react as described under 16: 0.47 g (71%) of **14h** as a colorless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 2.88 (dd, *J* = 15.5 and 11.3 Hz, 1H), 3.16–3.24 (m, 2H), 7.10–7.58 (m, 9H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –9.4, 29.8, 39.9, 122.2, 124.7, 126.7, 128.5, 128.8, 129.1, 131.5, 139.8, 140.4. – $C_{18}H_{21}F_3SSn$ (445.1): calcd. C 48.58, H 4.76; found C 48.75, H 4.90.

18. *1-(4-Methoxyphenylthio)-2-phenyl-1-trimethylstannylethane* (**14i**): To a solution of 0.56 g (2.0 mmol) of bis(4-methoxyphenyl) disulfide in 40 ml of methanol was added under nitrogen 0.27 g (7.0 mmol) of $NaBH_4$ in small portions over 1 h. Then 0.47 g (1.4 mmol) of **13** was added and the reaction was continued as described under 16. to give 0.43 g (78%) of **14i** as a slightly yellowish oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 2.88 (dd, *J* = 13.5 and 10.2 Hz, 1H), 3.06 (dd, *J* = 10.2 and 5.0 Hz, 1H), 3.24 (dd, *J* = 13.5 and 5.0 Hz, 1H), 3.83 (s, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.13–7.28 (m, 5H), 7.42 (d, *J* = 8.8 Hz, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –9.4, 33.0, 40.2, 55.3, 114.5, 126.3, 128.0, 128.3, 128.8, 132.9, 140.9, 158.8. – $C_{18}H_{24}OSSn$ (407.2): calcd. C 53.10, H 5.94; found C 53.28, H 6.00.

19. *2-Phenyl-1-(2,3,5,6-tetramethylphenylthio)-1-trimethylstannylethane* (**14j**): 0.69 g (2.1 mmol) of bis(2,3,5,6-tetramethylphenyl) disulfide[35] and 0.49 g (1.4 mmol) of **13** were allowed to react as described under 18. to give 0.44 g (72%) of **14j** as a slightly yellowish solid, m.p. 73 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.01 (s, 9H), 2.24 (s, 6H), 2.53 (s, 6H), 2.73–2.97 (m, 3H), 6.09 (s, 1H), 6.92–7.20 (m, 5H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –9.6, 18.7, 20.9, 33.3, 40.3, 126.2, 128.3, 128.6, 131.6, 134.0, 135.2, 138.5, 141.3. – $C_{21}H_{30}SSn$ (394.9): calcd. C 58.22, H 6.38; found C 58.19, H 6.54.

20. *2-Phenyl-1-phenylseleno-1-trimethylsilylethane* (**15k**): To a solution of 1.02 g (2.4 mmol) of **5** in 25 ml of anhydrous THF was added at –78 °C 1.7 ml (2.5 mmol) of a 1.4 M solution of *n*-butyllithium in hexane. After stirring for 10 min a solution of 0.27 g (2.5 mmol) of chlorotrimethylsilane in 5 ml of THF was slowly added. After stirring for 2 h the mixture was allowed to reach room temp. and then diluted with 100 ml of petroleum ether. The solution was washed three times with 30 ml of 7% aqueous KOH each and once with 20 ml of brine. The organic phase was dried with $MgSO_4$ and concentrated i.vac. Flash chromatography of the residue with petroleum ether furnished 0.72 g (88%) of **15k** as a slightly yellowish oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 2.58 (dd, *J* = 8.9 and 6.5 Hz, 1H), 2.84 (dd, *J* = 14.2 and 8.9 Hz, 1H), 3.10 (dd, *J* = 14.2 and 6.5 Hz, 1H), 7.04–7.21 (m, 10H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.9, 34.5, 38.7, 126.1, 126.7, 128.1, 128.7, 129.1, 131.4, 133.5, 141.4. – $C_{17}H_{22}SeSi$ (333.4): calcd. C 61.12, H 6.65; found C 61.07, H 6.74.

21. *1-(Dimethylphenylsilyl)-2-phenyl-1-phenylselenoethane* (**15l**): 1.12 g (2.69 mmol) of **5** and 0.47 g (2.8 mmol) of chlorodimethylphenylsilane were allowed to react as described under 20. Flash chromatography furnished 0.87 g (79%) of **15l** as a colorless oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.34 (s, 3H), 0.36 (s, 3H), 2.73 (dd, *J* = 9.8 and 4.8 Hz, 1H), 2.81 (dd, *J* = 13.6 and 9.8 Hz, 1H), 3.14 (dd, *J* = 13.6 and 4.8 Hz, 1H), 7.03–7.56 (m, 15H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.8, –3.2, 34.4, 38.6, 126.1, 126.8, 127.8, 128.0, 128.6, 129.2, 129.3, 131.5, 133.6, 134.1, 141.2. – $C_{22}H_{24}SeSi$ (395.5): calcd. C 66.82, H 6.12; found C 66.72, H 6.13.

22. *1-(Methyldiphenylsilyl)-2-phenyl-1-phenylselenoethane* (**15m**): 1.01 g (2.42 mmol) of **5** and 0.57 g (2.5 mmol) of chloromethyldiphenylsilane were allowed to react as described under 20. to give

0.80 g (72%) of **15m** as a colorless oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.64 (s, 3H), 2.79 (dd, *J* = 14.0 and 10.4 Hz, 1H), 2.96 (dd, *J* = 10.4 and 4.1 Hz, 1H), 3.29 (dd, *J* = 14.0 and 4.1 Hz, 1H), 6.98–7.60 (m, 20H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.6, 33.4, 38.8, 126.1, 126.8, 127.6, 127.8, 127.9, 128.0, 128.5, 129.3, 129.47, 129.54, 131.7, 133.6, 134.0, 135.0, 141.1, 142.3. – $C_{27}H_{26}SeSi$ (457.6): calcd. C 70.88, H 5.73; found C 70.99, H 6.03.

23. *2-Phenyl-1-phenylseleno-1-triphenylsilyl-ethane* **15n**: 1.01 g (2.43 mmol) of **5** and 0.72 g (2.4 mmol) of chlorotriphenylsilane were allowed to react as described under 20. to give 1.14 g (90%) of **15n** as a colorless oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.96 (dd, *J* = 14.3 and 11.0 Hz, 1H), 3.26 (dd, *J* = 11.0 and 3.4 Hz, 1H), 3.46 (dd, *J* = 14.3 and 3.4 Hz, 1H), 6.81–7.58 (m, 25H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.4, 39.7, 126.1, 126.7, 127.9, 128.0, 128.5, 129.5, 129.7, 132.1, 133.2, 133.7, 136.2, 141.0. – $C_{32}H_{28}SeSi$ (519.6): calcd. C 73.97, H 5.43; found C 74.00, H 5.32.

24. *1-[Dimethyl-(2,4,6-trimethylphenyl)silyl]-2-phenyl-1-phenylselenoethane* (**15o**): 0.98 g (2.4 mmol) of **5** and 0.53 g (2.5 mmol) of chlorodimethyl-(2,4,6-trimethylphenyl)silane[36] were allowed to react as described under 20. to give 0.79 g (77%) of **15o** as a colorless oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.40 (s, 3H), 0.53 (s, 3H), 2.24 (s, 3H), 2.38 (s, 6H), 2.87 (dd, *J* = 13.6 and 9.5 Hz, 1H), 3.02 (dd, *J* = 9.5 and 5.3 Hz, 1H), 3.14 (dd, *J* = 13.6 and 5.3 Hz, 1H), 6.75 (s, 2H), 7.04–7.14 (m, 10H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.1, 2.2, 20.9, 24.9, 35.9, 38.8, 126.0, 126.7, 128.0, 128.5, 129.0, 129.3, 131.0, 131.6, 133.7, 138.8, 141.3, 144.5. – $C_{25}H_{30}SeSi$ (437.5): calcd. C 68.64, H 6.91; found C 68.40, H 7.02.

25. *NMR Measurements:* An NMR tube was cleaned with hydrochloric acid, water, acetone, and ether. While blowing a stream of dry nitrogen through the tube heat was applied with a hot air gun. When the tube had again reached room temp. the starting material was weighed into the NMR tube which was closed with a septum cap. The septum cap was sealed with parafilm. Argon was passed through the tube by introducing two hypodermic needles. One needle was removed and 100 µl of the solvent (usually [D_8]THF) was injected by means of a dry gas-tight syringe. The starting material was dissolved in the liquid and further 500 µl of the solvent was injected in such a manner as to wash the inner walls of the tube. The tube was cooled in a dry ice/acetone bath. After 5 min a solution of *tert*-butyllithium in either [D_{12}]cyclohexane or [D_6]benzene was added by means of a gas-tight syringe. The *tert*-butyllithium solution solidified at the inner wall of the tube. The tube was briefly removed then from the cooling bath in order to liquefy part of the butyllithium solution, then vigorously shaken for 10 s and immediately recooled to –78 °C. This was repeated until all of the *tert*-butyllithium had dissolved. The tube was stored at –78 °C until the measurements were begun. In addition to the ^{1}H-NMR signals of the desired organolithium compound the sample showed signals of the coproduct, *tert*-butyl phenyl selenide, at δ = 1.40 and 7.21–7.52, or of trimethyl-*tert*-butylstannane at δ = 0.00 and 1.06. Proton chemical shifts were referenced to the residual proton signal of [D_8]THF at δ = 3.58.

After the NMR experiment the organolithium compound generated was treated either with diphenyl diselenide in the cases of **6**, **7k**–**7o**, or with trimethyltin chloride in the cases of **7g**–**7j** at –78 °C in order to regenerate the starting material. This was verified by NMR spectroscopy. In the cases of **7d** and **7f** the samples were treated with CH_3I. The resulting ^{1}H-NMR spectra were consistent with the formation of 2-arylseleno-1-phenylpropanes.

6: From **5** in [D_8]THF and *tert*-butyllithium in cyclopentane; ^{1}H NMR (500 MHz, 213 K): δ = 2.13 (dd, *J* = 10.1 and 3.7 Hz, 1H), 2.89 (broad t, *J* = 11.2 Hz, 1H), 3.40 (dd, *J* = 12.1 and 3.7 Hz, 1H).

7a: From **9a** in [D_8]THF and *tert*-butyllithiumin [D_6]benzene; ^{1}H NMR 500 (MHz, 223 K): δ = 1.97 (dd, *J* = 10.2 and 3.6 Hz, 1H), 2.88 (dd, *J* = 12.2 and 11.2 Hz, 1H), 3.42 (dd, *J* = 12.2 and 3.5 Hz, 1H).

7b: From **9b** in [D_8]THF and *tert*-butyllithium in [D_6]benzene; ^{1}H NMR (500 MHz, 223 K): δ = 2.18 (dd, *J* = 10.2 and 4.1 Hz, 1H), 2.96 (dd, *J* = 11.9 and 11.9 Hz, 1H), 3.42 (dd, *J* = 11.9 and 3.7 Hz, 1H).

7c: From **9c** in [D_8]THF and *tert*-butyllithium in [D_6]benzene; ^{1}H NMR (500 MHz, 213 K): δ = 2.03 (dd, *J* = 10.8 and 4.9 Hz, 1H), 2.90 (dd, *J* = 12.1 and 11.3 Hz, 1H), 3.01 (dd, *J* = 12.1 and 5.0 Hz, 1H).

7d: From **9d** in [D_8]THF and *tert*-butyllithium in [D_6]benzene; ^{1}H NMR (500 MHz, 193 K): δ = 1.93 (dd, *J* = 10.8 and 4.8 Hz, 1H), 2.82 (dd, *J* = 11.4 and 11.4 Hz, 1H), 2.89 (dd, *J* = 11.4 and 4.8 Hz, 1H).

7e: From **9e** in [D_8]THF and *tert*-butyllithium in [D_6]benzene; ^{1}H NMR (500 MHz, 203 K): δ = 2.60 (dd, *J* = 10.3 and 3.2 Hz, 1H), 3.32 (dd, *J* = 12.6 and 11.4 Hz, 1H), 3.66 (dd, *J* = 12.6 and 4.3 Hz, 1H).

7f: From **9f** in [D_8]THF and *tert*-butyllithium in [D_6]benzene; ^{1}H NMR (500 MHz, 203 K): δ = 2.49 (dd, *J* = 9.8 and 6.4 Hz, 1H), 3.19 (dd, *J* = 12.2 and 6.3 Hz, 1H), 3.23 (dd, *J* = 12 Hz, 1H).

7g: From **14g** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 213 K, decoupled at δ = 1.50): δ = 2.69 (d, *J* = 12.5 Hz, 1H), 3.29 (d, *J* = 12.5 Hz, 1H).

7h: From **14h** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 183 K): δ = 1.43 (broad d, *J* = 9.2 Hz, 1H), 2.66 (t, *J* = 10.4 Hz, 1H), 3.21 (broad d, *J* = 10 Hz, 1H).

7i: From **14i** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 203 K): δ = 1.44 (dd, *J* = 9.2 and 3.5 Hz, 1H), 2.64 (broad t, *J* = 10.5 Hz, 1H), 3.15 (broad d, *J* = 9.7 Hz, 1H), 6.75 (broad d, *J* = 8.5 Hz, 2H), 6.97–7.20 (m, 7H).

7j: From **14j** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 215 K): δ = 1.22 (dd, *J* = 10.4 and 4.8 Hz, 1H), 2.17 (s, 6H), 2.53 (s, 6H), 2.68 (t, *J* = 11.8 Hz, 1H), 2.77 (dd, *J* = 12.1 and 4.8 Hz, 1H), 6.64 (s, 1H), 6.86–7.03 (m, 5H).

7k: From **15k** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 193 K, decoupled at δ = –1.11): δ = –0.26 (s, 9H), 3.07 (d, *J* = 15.6 Hz, 1H), 3.21 (d, *J* = 15.6 Hz, 1H).

7l: From **15l** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 193 K): δ = –0.79 (dd, *J* = 9.6 and 5.2 Hz, 1H), –0.02 (s, 3H), 0.00 (s, 3H), 3.15 (dd, *J* = 15.0 and 9.6 Hz, 1H), 3.21 (dd, *J* = 15.0 and 5.2 Hz, 1H).

7m: From **15m** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 203 K): δ = –0.47 (broad t, *J* = 7.2 Hz, 1H), 0.30 (s, 3H), 3.18–3.24 (broad m, 2H).

7n: From **15n** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 193 K): δ = –0.23 (broad t, *J* = 6.8 Hz, 1H), 3.22 (dd, *J* = 15.0 and 7.8 Hz, 1H), 3.34 (dd, *J* = 15.0 and 6.3 Hz, 1H).

7o: From **15o** in [D_8]THF and *tert*-butyllithium in [D_{12}]cyclohexane; ^{1}H NMR (400 MHz, 223 K): δ = –0.72 (broad dd, *J* = 10 and 5 Hz, 1H), –0.03 (s, 3H), 0.24 (s, 3H), 2.15 (s, 3H), 2.45 (s, 6H), 3.13 (broad m, 2H), 6.58 (s, 2H), 6.85–7.63 (m, 5H).

11: From 1-phenyl-2-di(phenylseleno)propane in [D_8]THF and *tert*-butyllithium in [D_6]benzene; ^{1}H NMR (500 MHz, 173 K): δ = 1.49 (s, 3H), 2.46 (d, *J* = 11.5 Hz, 1H), 3.31 (d, *J* = 11.5 Hz, 1H).

[1] For part XV see: H. C. Stiasny, R. W. Hoffmann, *Chem. Eur. J.*, in press.

[2] D. Seebach, *Angew. Chem.* **1979**, *91*, 259–278; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239–258.

[3] [3a] W. C. Still, C. Sreekumar, *J. Am. Chem. Soc.* **1980**, *102*, 1201–1202. – [3b] J. S. Sawyer, T. L. Macdonald, G. J. McGarvey, *J. Am. Chem. Soc.* **1984**, *106*, 3376–3377. – [3c] P. Lesimple, J.-M. Beau, P. Sinay, *J. Chem. Soc., Chem. Commun.* **1985**, 894–895. – [3d] S. D. Rychnowsky, D. E. Mickus, *Tetrahedron Lett.* **1989**, *30*, 3011–3014. – [3e] D. S. Matteson, P. B. Tripathy, A. Sarkar, K. M. Sadhu, *J. Am. Chem. Soc.* **1989**, *111*, 4399–4402. – [3f] J. M. Chong, E. K. Mar, *Tetrahedron Lett.* **1990**, *31*, 1981–1984. – [3g] P. C.-M. Chan, J. M. Chong, *Tetrahedron Lett.* **1990**, *31*, 1985–1988. – [3h] D. Hoppe, F. Hintze, P. Tebben, *Angew. Chem.* **1990**, *102*, 1457–1458; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1422–1423.

[4] [4a] R. J. Linderman, B. D. Griedel, *J. Org. Chem.* **1991**, *56*, 5491–5493. – [4b] R. Hoffmann, R. Brückner, *Chem. Ber.* **1992**, *125*, 2731–2739. – [4c] S. D. Rychnovsky, D. J. Skalitzky, *J. Org. Chem.* **1992**, *57*, 4336–4339. – [4d] M. Paetow, H. Ahrens, D. Hoppe, *Tetrahedron Lett.* **1992**, *33*, 5323–5326. – [4e] H. Ahrens, M. Paetow, D. Hoppe, *Tetrahedron Lett.* **1992**, *33*, 5327–5330. – [4f] J. Schwerdtfeger, D. Hoppe, *Angew. Chem.* **1992**, *104*, 1547–1549; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1505–1507. – [4g] F. Hintze, D. Hoppe, *Synthesis* **1992**, 1216–1218. – [4h] P. Sommerfeld, D. Hoppe, *Synlett* **1992**, 764–766. – [4i] D. Hoppe, M. Paetow, F. Hintze, *Angew. Chem.* **1993**, *105*, 430–432; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 394–396. – [4j] J. Haller, T. Hense, D. Hoppe, *Synlett.* **1993**, 726–728. – [4k] S. D. Rychnovsky, K. Plzak, D. Pickering, *Tetrahedron Lett.* **1994**, *35*, 6799–6802. – [4l] W. Guarnieri, M. Grehl, D. Hoppe, *Angew. Chem.* **1994**, *106*, 1815–1818; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1734–1737.

[5] [5a] R. E. Gawley, G. C. Hart, L. J. Bartolotti, *J. Org. Chem.* **1989**, *54*, 175–181. – [5b] W. H. Pearson, A. C. Lindbeck, *J. Am. Chem. Soc.* **1991**, *113*, 8546–8548. – [5c] S. T. Kerrick, P. Beak, *J. Am. Chem. Soc.* **1991**, *113*, 9708–9710. – [5d] T. T. Shawe, A. I. Meyers, *J. Org. Chem.* **1991**, *56*, 2751–2755. – [5e] J. M. Chong, S. B. Park, *J. Org. Chem.* **1992**, *57*, 2220–2222. – [5f] A. I. Meyers, G. Milot, *J. Am. Chem. Soc.* **1993**, *115*, 6652–6660. – [5g] W. H. Pearson, A. C. Lindbeck, J. W. Kampf, *J. Am. Chem. Soc.* **1993**, *115*, 2622–2636. – [5h] R. E. Gawley, Q. Zhang, *J. Am. Chem. Soc.* **1993**, *115*, 7515–7516. – [5i] A. F. Burchat, J. M. Chong, S. B. Park, *Tetrahedron Lett.* **1993**, *34*, 51–54. – [5j] P. Beak, S. T. Kerrick, S. Wu, J. Chu, *J. Am. Chem. Soc.* **1994**, *116*, 3231–3239. – [5k] D. L. Comins, N. R. Benjelloun, *Tetrahedron Lett.* **1994**, *35*, 829–832.

[6] P. G. McDougal, B. D. Condon, M. D. Laffosse Jr., A. M. Lauro, D. VanDerveer, *Tetrahedron Lett.* **1988**, *29*, 2547–2550.

[7] H. J. Reich, M. D. Bowe, *J. Am. Chem. Soc.* **1990**, *112*, 8994–8995.

[8] G. P. Lutz, A. P. Wallin, S. T. Kerrick, P. Beak, *J. Org. Chem.* **1991**, *56*, 4938–4943.

[9] [9a] A. Krief, G. Evrard, E. Badaoui, V. De Beys, R. Dieden, *Tetrahedron Lett.* **1989**, *30*, 5635–5638. – [9b] R. W. Hoffmann, M. Bewersdorf, *Liebigs Ann. Chem.* **1992**, 643–653. – [9c] A. Krief, E. Badaoui, W. Dumont, *Tetrahedron Lett.* **1993**, *34*, 8517–8520.

[10] [10a] R. H. Ritter, T. Cohen, *J. Am. Chem. Soc.* **1986**, *108*, 3718–3725. – [10b] K. Brickmann, R. Brückner, *Chem. Ber.* **1993**, *126*, 1227–1239. – [10c] W. Klute, R. Dress, R. W. Hoffmann, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1409–1411. – [10d] K. Brickmann, F. Hamblock, E. Spolaore, R. Brückner, *Chem. Ber.* **1994**, *127*, 1949–1957. – [10e] R. W. Hoffmann, M. Julius, F. Chemla, T. Ruhland, G. Frenzen, *Tetrahedron* **1994**, *50*, 6049–6060.

[11] [11a] T. Clark, P. v. R. Schleyer, J. A. Pople, *J. Chem. Soc., Chem. Commun.* **1978**, 137–138. – [11b] E. Kaufmann, K. Raghavachari, A. E. Reed, P. v. R. Schleyer, *Organometallics* **1988**, *7*, 1597–1607.

[12] H. J. Reich, M. A. Medina, M. D. Bowe, *J. Am. Chem. Soc.* **1992**, *114*, 11003–11004.

[13] [13a] N. D. Epiotis, R. L. Yates, F. Bernardi, S. Wolfe, *J. Am. Chem. Soc.* **1976**, *98*, 5435–5439. – [13b] J.-M. Lehn, G. Wipff, *J. Am. Chem. Soc.* **1976**, *98*, 7498–7505. – [13c] J. M. Lehn, G. Wipff, J. Demunynck, *Helv. Chim. Acta* **1977**, *60*, 1239–1246. – [13d] P. v. R. Schleyer, A. J. Kos, *Tetrahedron* **1983**, *39*, 1141–1150. – [13e] P. v. R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk, N. G. Rondan, *J. Am. Chem. Soc.* **1984**, *106*, 6467–6475.

[14] D. Seebach, N. Meyer, A. K. Beck, *Liebigs Ann. Chem.* **1977**, 846–858.

[15] Cryoscopic determinations were made by F. Haller, Dissertation Universität Marburg, **1994**, essentially using an apparatus described by W. Bauer, D. Seebach, *Helv. Chim. Acta* **1984**, *67*, 1972–1988.

[16] [16a] G. Fraenkel, M. Henrichs, J. M. Hewitt, B. M. Su, M. J. Geckle, *J. Am. Chem. Soc.* **1980**, *102*, 3345–3350. – [16b] G. Fraenkel, M. Henrichs, M. Hewitt, B. M. Su, *J. Am. Chem. Soc.* **1984**, *106*, 255–256.

[17] Osmometric determinations of the aggregation state were based on the techniques developed by T. West, R. Waack, *J. Am. Chem. Soc.* **1967**, *89*, 4395–4399; for details of the measurements see A. Wenzel, Diplomarbeit Universität Marburg, **1994**.

[18] G. Binsch, *Top. Stereochem.* **1967**, *3*, 97–192.

[19] J. Heinzer, J. F. M. Oth, D. Seebach, *Helv. Chim. Acta* **1985**, *68*, 1848–1862.

[20] [20a] A. Streitwieser jr., C. J. Chang, W. B. Hollyhead, J. R. Murdoch, *J. Am. Chem. Soc.* **1972**, *94*, 5288–5291. – [20b] E. Buncel, B. C. Menon, *J. Org. Chem.* **1979**, *44*, 317–320. – [20c] D. H. O'Brien, C. R. Russel, A. J. Hart, *J. Am. Chem. Soc.* **1979**, *101*, 633–639.

[21] W. Zarges, M. Marsch, K. Harms, W. Koch, G. Frenking, G. Boche, *Chem. Ber.* **1991**, *124*, 543–549.

[22] K. B. Wiberg, H. Castejon, *J. Am. Chem. Soc.* **1994**, *116*, 10489–10497, and references quoted.

[23] R. K. Dress, T. Rölle, R. W. Hoffmann, *Chem. Ber.* **1995**, *128*, 673–677.

[24] [24a] J. E. Wollrab, V. W. Laurie, *J. Chem. Phys.* **1968**, *48*, 5058–5066. – [24b] cf. also: J. D. Swalen, J. A. Ibers, *J. Chem. Phys.* **1962**, *36*, 1914–1918. – [24c] C. C. Costain, G. B. B. M. Sutherland, *J. Phys. Chem.* **1952**, *56*, 321–324.

[25] In response to a referee's comment regarding rotation about the $C^{-}-CH_2Ph$ bond, we do not believe this step to be rate-limiting for the enantiomerization of **6**, because very similar activation barriers were found for the enantiomerization of the corresponding $C^{-}-CH_2CH(CH_3)_2$-compound[10c].

[26] [26a] H.-J. Gais, G. Hellmann, H. Günther, F. Lopez, H. J. Lindner, S. Braun, *Angew. Chem.* **1989**, *101*, 1061–1063; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1025–1027. – [26b] H.-J. Gais, G. Hellmann, *J. Am. Chem. Soc.* **1992**, *114*, 4439–4440.

[27] G. Fraenkel, W. R. Winchester, P. G. Willard, *Organometallics* **1989**, *8*, 2308–2311.

[28] H. J. Reich, R. R. Dykstra, *Angew. Chem.* **1993**, *105*, 1489–1491; *Angew. Chem. Int. Ed. Engl.* **1993**, *23*, 1469–1470.

[29] R. Amstutz, T. Laube, W. B. Schweitzer, D. Seebach, J. D. Dunitz, *Helv. Chim. Acta* **1984**, *67*, 224–236.

[30] J. E. Leffler, *J. Org. Chem.* **1955**, *20*, 1202–1231.

[31] Our data do not pass the rigorous statistical tests for an isokinetic relationship (W. Linert, R. F. Jameson, *Chem. Soc. Rev.* **1989**, *18*, 477–505; W. Linert, *Chem. Soc. Rev.* **1994**, *23*, 429–438) which, however, is not what we want to prove. We want to apply this $\Delta H^{+}/\Delta S^{+}$ correlation to identify families of reactions passing through the same type of rate-limiting transition state.

[32] cf. M. Clarembeau, A. Cravador, W. Dumont, L. Hevesi, A. Krief, J. Lucchetti, D. Van Ende, *Tetrahedron* **1985**, *41*, 4793–4812.

[33] D. Seebach, A. K. Beck, *Chem. Ber.* **1975**, *108*, 314–321.

[34] H. J. Reich, W. W. Willis, jr., P. D. Clark, *J. Org. Chem.* **1981**, *46*, 2775–2784.

[35] G. Illuminati, *J. Am. Chem. Soc.* **1958**, *80*, 4945–4948.

[36] H. Müller, U. Weinzierl, W. Seidel, *Z. Anorg. Allg. Chem.* **1991**, *603*, 15–20.

[95049]