α-Oxygen-Substituted Organolithium Compounds and Their Carbenoid Nature: Calculations of the Configurational Stability and of $LiCH_2OH$ Model Structures, Crystal Structure of Diphenyl(trimethylsilyloxy)methyllithium · 3 THF, and the Stereochemistry of the (Reverse) Brook Rearrangement[☆]

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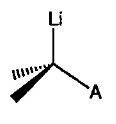
The comparatively high configurational stability of α-oxygen-substituted organolithium compounds is confirmed by ab initio calculations [MP2/6-311++G(d,p)]. Model calculations of the $LiCH_2OH$ structures **21A–D** (MP2/6-31G(d)//3-21G and MP2/6-311++G(d,p)//MP2/6-311++G(d,p)) are in agreement with recently determined crystal structures of α-oxygen-substituted organolithium compounds. They also suggested the preparation of a new structural type (**21C**) which has been verified by means of diphenyl(trimethylsilyloxy)methyllithium · 3 THF (**24** · 3 THF) as shown by X-ray crystallography. The *lengthening* of the C–O bonds in all four α-oxygen-substituted organolithium compounds known to date contrasts strongly with the wealth of structural data from organolithium compounds α-substituted with "typical" acceptor substituents: on lithiation the carbon-acceptor bond length in these compounds is always *shortened*. This difference is in agreement with a *carbenoid character* of α-oxygen-substituted organolithium species. Finally, the crystal structure of **24** · 3 THF serves as a model for the surprising stereochemistry of the (reverse) Brook rearrangement.

1. Introduction

In contrast to the enormous importance of organolithium compounds in organic synthesis, structural informations about these compounds became available only in the last decade. Seebach has summarized the results on lithium enolates[1], and we have reviewed the structures of lithium sulfones, sulfoximides, sulfoxides, thioethers, dithianes, nitriles, nitro compounds, and hydrazones[2]. Evidently, in both cases one is dealing with "carbanions" stabilized by typical acceptor substituents A.

Scheme 1



Typical acceptor substituents A :
C(O)R, SO_2R, SO(NR)R, S(O)R, SR, CN, NO_2, C(N-NR)R

Atypical acceptor substituents A :
OR, NR_2, halogen

In contrast to this class of compounds not much is known about the structures of organolithium species with atypical acceptor substituents (A = OR, NR_2, halogen) at the anionic carbon atom[3,4], although they have long been known and are widely used in synthesis. The importance of α-oxygen-substituted organolithiums – the topic of this investigation – is illustrated by the following examples (see Table 1): the 1,2-Wittig rearrangement **1**→**2**[5]; Still's

Table 1. Some preparations and reactions of α-oxygen-substituted organolithium compounds (Cb and Cbx: different carbamoyl groups)

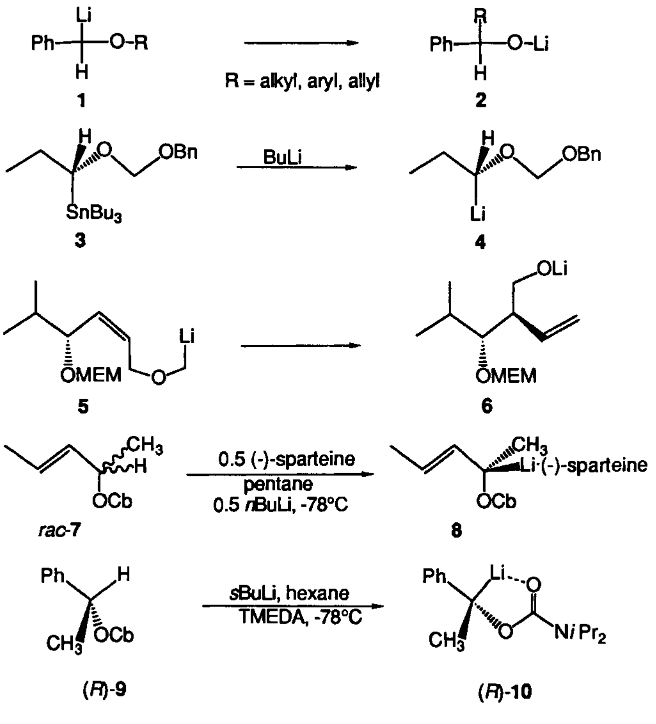
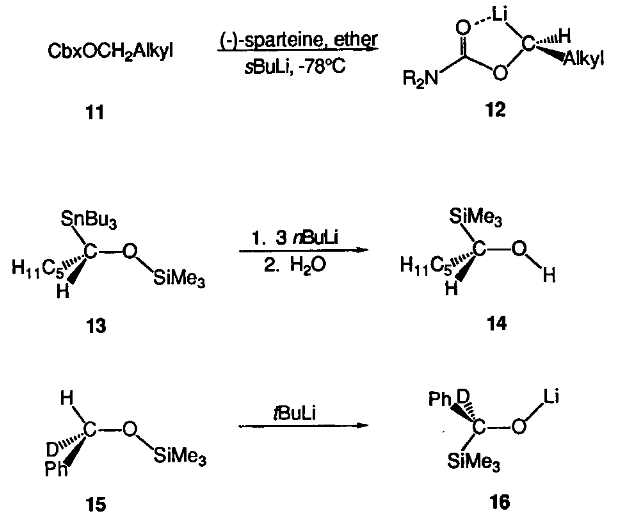


Table 1 *(Continued)*



11 **12**

13 **14**

15 **16**

synthetically important discovery of the stereoselective access of the configurationally comparatively stable alkoxy-substituted compounds **4** from **3** and the retention of configuration in their reactions with electrophiles[6]; the stereoselective 2,3-Wittig rearrangement **5**→**6**[7]; the stereoselective preparation of carbamoyloxy-substituted allyl- (**7**→**8**)[8], benzyl- (**9**→**10**)[9], and alkyllithium compounds (**11**→**12**)[10] by Hoppe; and the stereoselective reverse Brook rearrangement with alkyl (**13**→**14**)[11] and aryl substituents (**15**→**16**)[12] at the anionic carbon atoms, with the remarkable feature that the former occurs with complete retention of configuration (99%), while 99% inversion of configuration is observed in the latter[13].

At present, three crystal structure determinations of α-oxygen-substituted organolithium compounds have been published: [2-benzofuryllithium · TMEDA]$_2$ {[**17** · TMEDA]$_2$}[14], [2-lithio-3-bromobenzofuran · diisopropylether]$_2$ {[**18** · O-(*i*Pr)$_2$]$_2$}[15], and η^1-(1*S*,2*E*)-1-(*N*,*N*-diisopropylcarbamoyloxy)-3-trimethylsilylallyllithium · (−)-sparteine (**19** · sparteine)[16]. In the first two cases the lithium ion bridges the anionic carbon atom and the oxygen atoms (in [**17** · TMEDA]$_2$ only one such bridge is observed), while in **19** · sparteine

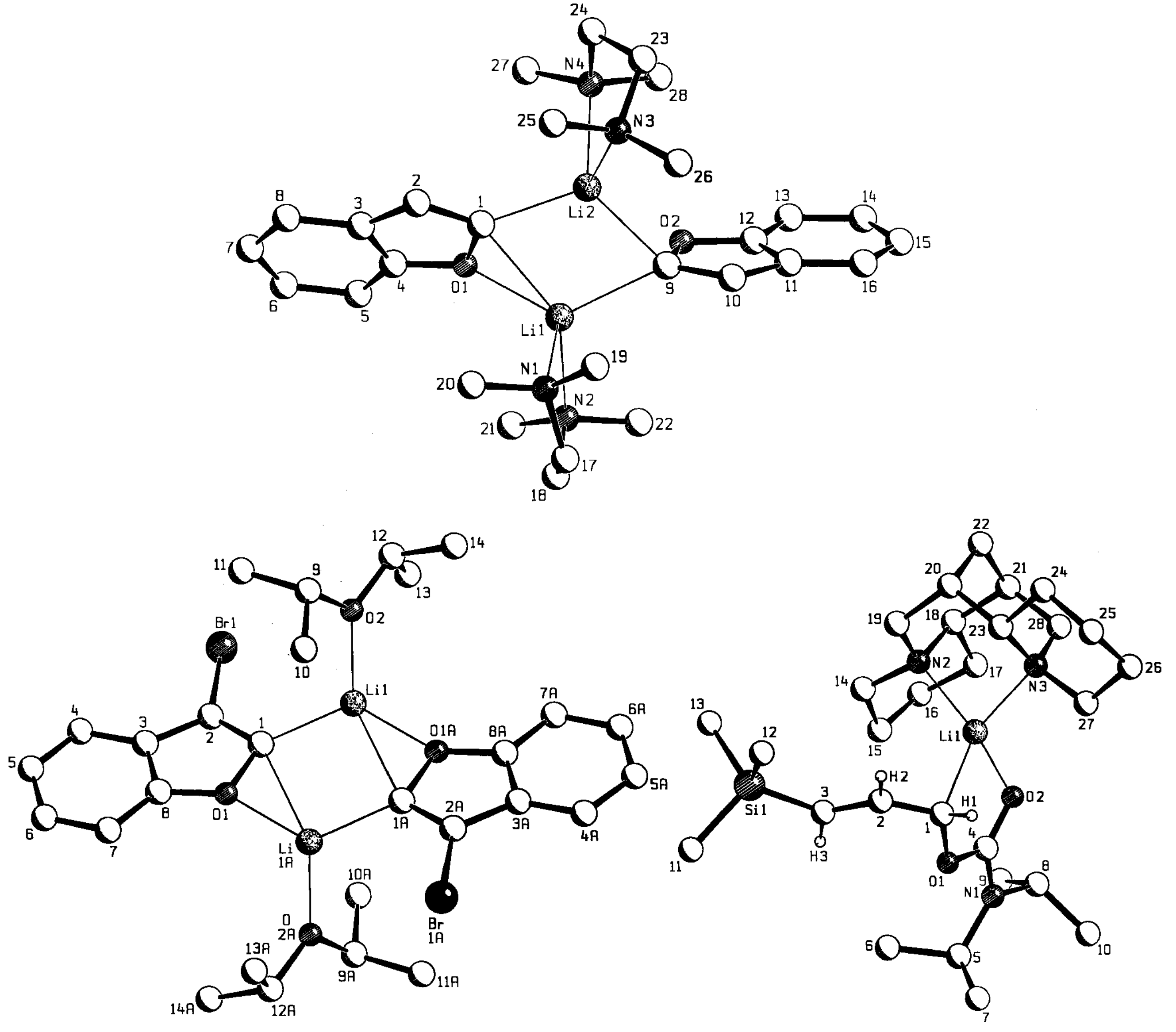


Figure 1. Crystal structures of [**17** · TMEDA]$_2$ (top), [**18** · O(*i*Pr)$_2$]$_2$ (left), and **19** · sparteine (right)

lithium is η¹-bonded to the pyramidalized, oxygen-substituted allylic carbon atom (see Figure 1).

In this paper we wish to demonstrate how (i) a theoretical study of the structural isomers of lithiated methanol $LiCH_2$-OH together with the structures of $[\mathbf{17}\cdot TMEDA]_2$, $[\mathbf{18}\cdot O(iPr)_2]_2$, and $\mathbf{19}\cdot$ sparteine led to the search for a species with the structural characteristics found in the title compound diphenyl(trimethylsilyloxy)methyllithium · 3 THF (**24** · 3 THF); (ii) an oxygen substituent RO– stabilizes a negative charge at the α-carbon atom; (iii) the X-ray structure of the title compound serves as a model to explain the surprising stereochemistry of the (reverse) Brook rearrangement (as indicated by the transformations **13**→**14** and **15**→**16**); and (iv) theoretical calculations agree with the comparatively high configurational stability of α-oxygen-substituted organolithium compounds.

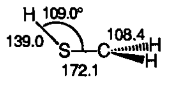
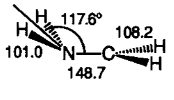
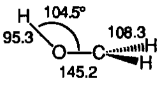
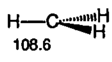
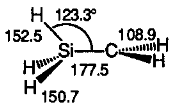
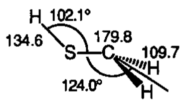
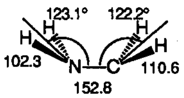
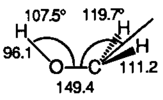
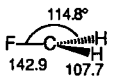
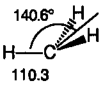
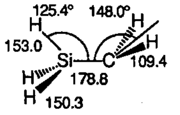
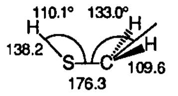
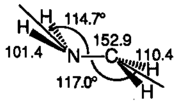
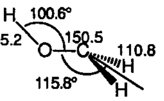
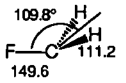
2. Results and Discussion

2.1. Model Calculations of the Configurational Stability of the (Substituted) Methyl Anion

The relatively high and synthetically important configurational stability of alkoxy-substituted organolithium compounds as discovered by Still[6a], and as also observed in other cases[6b–f,7–13], raises the question about the size of and the reason for this unusual property. Therefore, we calculated the energies of the methyl anion $^-CH_2-H$ (**20-H**) and of the substituted methyl anions $^-CH_2-SiMe_3$ (**20-SiH$_3$**), $^-CH_2-SH$ (**20-SH**), $^-CH_2-NH_2$ (**20-NH$_2$**), $^-CH_2-OH$ (**20–OH**), and $^-CH_2-F$ (**20-F**) in the planar and in the more stable pyramidal configurations. The energy difference between the most stable pyramidal and the planar configuration ("inversion energy") should be related to the configurational stability of the corresponding organometallic (organolithium) compound. The results are summarized in Table 2[17–20].

The computational data of Table 2 correspond nicely to experimental results of organolithium species. In the case of the methyl anion **20-H** the energy difference between the two configurations (3.0 kcal/mol) is in agreement with the difficulty to prepare configurationally stable organolithium compounds with normal alkyl substituents[21]. Small energy differences are also calculated for **20-SiH$_3$** (0.8 kcal/mol) and **20-SH** (2.8 kcal/mol). Indeed, sulfur-substituted organolithium compounds have been reported to be configurationally not very stable[22]. In contrast, much larger inversion energies have been calculated for **20-NH$_2$** (11.0 kcal/mol), **20-OH** (11.0 kcal/mol) and **20-F** (13.6 kcal/mol). The configurational stability of alkoxy-substituted organolithium compounds[6–13] is thus nicely supported by the model calculations of **20-OH**. Very recently, evidence for the configurational stability of nitrogen-substituted organolithium compounds was obtained[23], again confirming the calculations. The much higher configurational stability of **20-NH$_2$**, **20-OH**, and **20-F** compared to that of **20-H**, **20-SiH$_3$**, and **20-SH**, is due to (i) the stabilization of the pyramidal con-

Table 2. MP 2/6-311 + + G(d,p)//MP 2/6-311 + + G(d,p) energies in au and relative energies in kcal/mol of the (substituted) methyl anion; bond lengths are in pm

20-H	**20-SiH$_3$**	**20-SH**	**20-NH$_2$**	**20-OH**	**21-F**
		 H-C-H: 120.4° -437.52298 (+2.8)	 H-C-H: 123.0° H-N-H: 101.5° - 94.92832 (+11.0)	 H-C-H: 125.2° - 114.79081 (+11.0)	
 H-C-H: 120° -39.71222 (+3.0)	 H-C-H: 115.7° H-Si-H: 106.0° -330.08207 (+0.8)	 H-C-H: 109.5° -437.52563 (+1.1)	 H-C-H: 105.6° H-N-H: 103.7° - 94.93665 (+5.2)	 H-C-H: 106.5° - 114.80163 (+4.2)	 H-C-H: 130.4 - 138.79311 (+13.6)
 H-C-H: 109.2° -39.71707 (0)	 H-C-H: 112.5° H-Si-H: 105.8° -330.08333 (0)	 H-C-H: 111.1° -437.52742 (0)	 H-C-H: 104.6° H-N-H: 101.8° - 94.94599 (0)	 H-C-H: 105.5° - 114.80831 (0)	 H-C-H: 104.4° - 138.81484 (0)

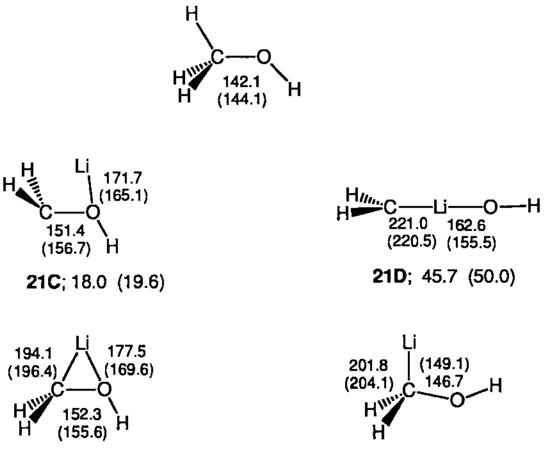
figuration in the former anions by the more electronegative substituents, and (ii) the destabilization of the planar configuration in these anions because of the repulsive interactions of the electron pairs at N, O, and F with the electron pair at the anionic C in the planar configuration[18,19].

Not unexpectedly, a lower configurational stability is expected if the α-oxygen-substituted carbon atom is of the allylic[8] or benzylic type[9]. Hoppe reports on the "capricious stereochemistry" observed in the reactions of carbamoyloxy-substituted *benzyl*lithium compounds with electrophiles: depending on the electrophile, retention or inversion of configuration is found[9].

2.2. Calculated Structures of $LiCH_2OH$ and Crystal Structures of α-Oxygen-Substituted Organolithium Compounds

The first calculations of the $LiCH_2OH$ isomers **21A–D** have been performed by Clark, von Ragué Schleyer, Houk, and Rondan eleven years ago[24]. They have been stimulated by NMR investigations[25] and calculations[26] of carbenoids like $LiCH_2X$, $LiCHX_2$, $LiCX_3$, and others (X = *halide*)[27]. Table 3 summarizes the earlier structures **21A–D** of $LiCH_2OH$ [which, in principal, are very similar to those of the Li/halide carbenoids $LiCH_2F(Cl)$[26]], together with our higher level calculations.

Table 3. MP2/6-311++G(d,p)//MP2/6-311++G(d,p) calculated structures (bond lengths in pm) and relative energies (in kcal/mol) corrected to zero-point vibration of $LiCH_2OH$; the earlier MP2/6-31G(d) data[24] are given in parentheses

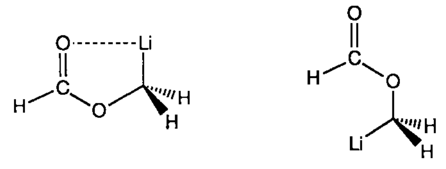


The carbon–oxygen-bridged isomer **21A** is the most stable one. The calculations predict a considerably longer C–O bond (152.3 pm) than in non-lithiated methanol CH_3OH (142.1 pm; the experimental value is 142.7 pm). Other[18,19] and our calculations of the anion $^-CH_2OH$ shown in Table 2 also predict a longer C–O bond (**20**-OH: 150.5 and 149.4 pm). The "classical"[24] nonbridged structure **21B** with the lithium ion being bound only to the anionic carbon atom is 14.0 kcal/mol higher in energy than **21A**. The C–O bond is less elongated (146.7 pm) than in **21A**. **21C** is 18.0 kcal/mol higher in energy than **21A** and has also a longer C–O bond (151.4 pm). In this isomer the lithium ion is only bound to the α-oxygen atom. There is another remarkable feature of **21C**: if one assumes that (i) lithiation occurs with retention of configuration (which has been amply demonstrated[6–13]) to give first isomer **21A** and/or **21B**, and (ii) **21C** is formed by suprafacial migration of the lithium ion from the carbon atom in **21A** and/or **21B** to the oxygen atom in **21C**, then the formation of **21C** involves an *inversion* of configuration at the anionic carbon atom. Structure **21D**, a metallocarbenium isomer, is rather energy-rich (45.7 kcal/mol above **21A**) and thus not very likely to be formed. However, it strongly indicates an *electrophilic* character of the carbon atom of α-oxygen-substituted "anions".

As far as these calculations and their relations to the known crystal structures of α-oxygen-substituted organolithium compounds (see Figure 1) are concerned, one immediately recognizes that the most stable calculated model structure **21A** agrees well with the experimental findings in [**17** · TMEDA]$_2$[14] and especially in [**18** · $O(iPr)_2$]$_2$[15]. In [**17** · TMEDA]$_2$ the lithium ion bridges C and O in one benzofuranyl anion although this leads to a pentacoordinated lithium ion. In both compounds one also finds longer C–O bonds (145.3[14] and 147.0 pm[15]) than in non-lithiated benzofuranes (mean value of 27 benzofurans: 138.5 pm[28]).

The "classical" structural type **21B** is found in the crystal structure of **19** · sparteine[16]. The substituents at the lithiated pyramidal carbon atom are bent away from the carbon–lithium bond. The C–O bond (147.6 pm) is elongated if compared to the C–O bonds in non-lithiated carbamoyl-oxy-substituted compounds: the mean value C_{sp^2}–OCb (six compounds) amounts to 139.6 pm; in the case of C_{sp^3}–OCb (11 compounds) this value is 143.6 pm[28,29]. Undoubtedly, **19** · sparteine overcomes its energetically more unfavorable "classical" lithium bonding situation (the model **21B** lies 14.0 kcal/mol above **21A**) by means of the five-membered ring lithium chelate formation with the oxygen atom of the carbamoyl group [Li–O: 189.7(8) pm], and by dipole stabilization[30]. Interestingly, model calculations indicate that in a related case the chelated species **22** is 13.2 kcal/mol more stable than the "open" isomer **23**[31] (Scheme 2).

Scheme 2



22; 0.0* **23**; 13.2*

* 4-31 G relative energies [kcal/mol].

The fact that η^3-allyllithium coordination[32] is also not observed in **19** · sparteine, additionally supports the favorable chelate (dipole) stabilization.

What are the structural requirements for an α-oxygen-substituted compound to exist in a structural type corresponding to the calculated $LiCH_2OH$ model **21C** (18.0 kcal/

mol above **21 A**) with the lithium ion only bonded to the oxygen atom? It has been shown in structural investigations of several (substituted) benzyllithium compounds[20,33] that *delocalization* of the negative charge leading to reduced charge density at the "anionic" carbon atom results in a reduced strength of the corresponding carbon–lithium bond, and thus allows the lithium cation to search for better bonding alternatives as – in the case of interest – an α-oxygen atom. This exactly is shown in the crystal structure of diphenyl(trimethylsilyloxy)methyllithium · 3 THF (**24** · 3 THF).

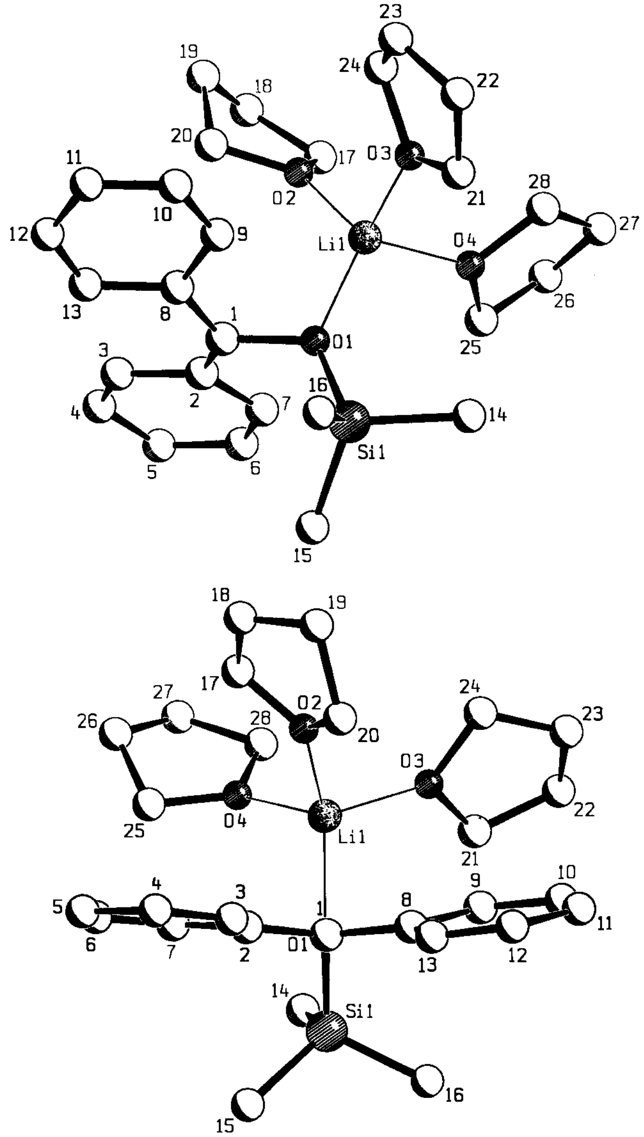


Figure 2. (a) Crystal structure of **24** · 3 THF (top); (b) view along the axis C1–O1 without the THF carbon atoms (bottom); selected bond lengths [pm], bond and torsional angles [°]: Li1–C1 280.7(2), C1–O1 148.8(8), C1–C8 143.9(12), C1–C2 138.5(12), O1–Si1 165.4(4), Li1–O1 198.4(14), Li1–O2 191.2(13), Li1–O3 196.5(16), Li1–O4 199.2(13); C2–C1–C8 134.2(7), O1–C1–C2 113.2(6), O1–C1–C8 111.5(6), Si1–O1–Li1 136.4(4), Si1–O1–C1 116.6(4); O1–C1–C2–C7 3(1), O1–C1–C8–C9 11(1), C8–C1–O1–Li1 –85.2(8), C8–C1–O1–Li1 84.6(8), C8–C1–O1–Si1 93.8(7), C2–C1–O1–Si1 –96.5(7)

2.3. The Crystal Structure of Diphenyl(trimethylsilyloxy)methyllithium · 3 THF (24 · 3 THF)

The crystal structure of diphenyl(trimethylsilyloxy)methyllithium · 3 THF (**24** · 3 THF) is shown in Figure 2a.

The distance between Li1 and C1 [280.7(2) pm] exceeds the length of carbon–lithium bonds (< 250 pm[1,2,20]) significantly. Thus, Li1 is only bound to O1 of the anion [148.8(8) pm] and to the oxygen atoms O2, O3 and O4 of the three tetrahydrofuran molecules. The charge delocalization into the two phenyl rings which weakens a possible carbon–lithium bond is well-documented by the upfield chemical shifts of the signals of the *ortho*- and *para*-phenyl carbon atoms in the ^{13}C-NMR spectrum of **24** in [D$_8$]THF, as compared to the non-lithiated diphenylmethyl trimethylsilyl ether (see Table 4).

Table 4. ^{13}C-NMR chemical shifts [pm] of **24** in [D$_8$]THF and diphenylmethyl trimethylsilyl ether in CDCl$_3$ at 298 K

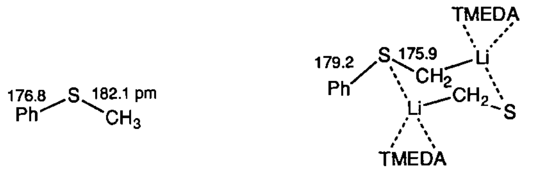
	24	1,1-Diphenylmethyl trimethylsilyl ether
C1	111.2	76.4
C_{ipso}	140.4	144.7
C_{ortho}	113.5	126.4
C_{meta}	128.2	128.1
C_{para}	107.1	126.0

The torsional angles O1–C1–C2–C7 [3(1)°] and O1–C1–C8–C13 [–170.6(7)°] are in agreement with a favorable charge delocalization into the phenyl rings. Inspite of this charge delocalization the two phenyl rings show some "inversion" as calculated for the LiCH$_2$OH model **21 C** (which of course is more pronounced there because of the hydrogen substituents, see Table 3): the torsional angles C2–C1–O1–Li1 [84.6(8)°] and C8–C1–O1–Li1 [–85.2(8)°] indicate that the phenyl rings are slightly bent towards the lithium ion (see Figure 2b). It is not clear whether deprotonation of diphenylmethyl trimethylsilyl ether first leads to structures of the type **21 A** and/or **21 B**, followed by suprafacial Li1 migration to O1 together with inversion at C1, or whether Li1 has never been in contact with C1. One can, however, imagine – even in the latter case – that deprotonation took place from the side at which Li1 is located, followed by inversion at C1. This rather unusual bonding situation in **24** · 3 THF will be of importance in the discussion of the strongly substituent-depending stereochemistry of the (reverse) Brook rearrangement (see section 2.4.). The C1–O1 bond in **24** · 3 THF [148.8(8) pm] is comparatively long. The mean (maximum) value of 135 C_{sp^3}–OSiMe$_3$ bonds[28] amounts to 140.2 (146.1) pm; the mean (maximum) value of 24 C_{sp^2}–OSiMe$_3$ bonds is even shorter [137.5 (142.8) pm]. Since C1 more closely resembles an sp^2- than an sp^3-hybridized carbon atom the experimental value [148.8(8) pm] should rather be compared with the mean sp^2 value (137.5 pm). A similar result has been found in the other structurally characterized α-oxygen-substituted organolithium compounds [**17** · TMEDA]$_2$, [**18** · O(iPr)$_2$]$_2$, and **19** · sparteine (see section 2.2.).

Thus, all experimental results so far known about these compounds confirm the calculations of the LiCH$_2$OH isomers **21 A–C** (Table 3) as well as those of the pyramidal anion $^-$CH$_2$OH (**20**-OH) (Table 2 and ref.[19]) concerning the C–O bond lengths in α-oxygen-substituted carbanions and organolithium compounds.

This is remarkable because in *all* the structures of organolithium compounds with a typical acceptor substituent [C(O)R, SO$_2$R, SO(NR)R, S(O)R, CN, NO$_2$, C(N–NR)R etc.] in α-position to the anionic carbon atom, *the bond between this atom and the substituent is shortened*[1,2], even so in α-*sulfur*-substituted organolithium compounds as shown by a comparison of methyl phenyl thioether (**25**) with the lithiated methyl phenyl thioether [**26** · TMEDA]$_2$[34].

Scheme 3



25 [**26**·TMEDA]$_2$

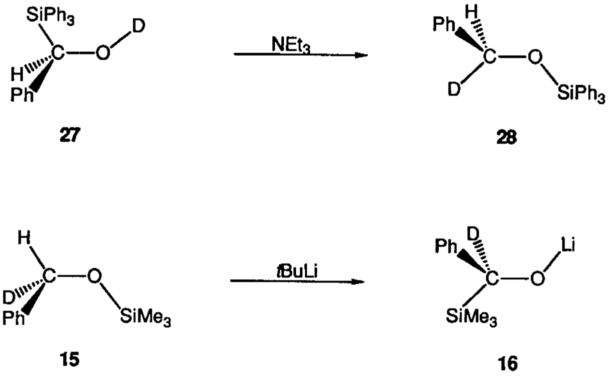
The mean value for H_3C-S bonds in thioethers like **25** amounts to 182.1 pm while the H_2C-S bond in the lithiated [**26** · TMEDA]$_2$ is only 175.9 pm long which is in agreement with the calculated data of **20**-SH in Table 2 and earlier calculations[18,19]. The $C_{Ph}-S$ bonds in **25** and [**26** · TMEDA]$_2$ are also of interest: the mean value in phenyl thioethers like **25** amounts to 176.8 pm; in [**26** · TMEDA]$_2$, however, this bond is elongated to 179.2 pm. A similar effect is *not* observed in **24** · 3THF: the O1 – Si1 bond length (165.4 pm) is essentially identical with the mean O – $SiMe_3$ bond length (165.3 pm) in 135 compounds with this structural element[28]. The structural differences between the oxygen-substituted **24** · 3THF and the sulfur-substituted [**26** · TMEDA]$_2$ nicely illustrate the different mechanisms of stabilizing a negative charge by oxygen and sulfur atom: in the case of a sulfur atom polarization and negative hyperconjugation are important; an oxygen atom, on the other hand, stabilizes a negative charge mainly by induction[18]. According to Bernardi[19] a sulfur atom stabilizes a negative charge better than an oxygen atom because of the different σ effects.

In summary: for the first time the *lengthening* of the C – acceptor bond in a compound with a lithiated carbon atom has been observed in the crystal structures of the α-oxygen-substituted organolithium compounds **24** · 3THF as well as [**17** · TMEDA]$_2$[14], [**18** · O(*i*Pr)$_2$]$_2$[15] and **19** · sparteine[16]. A similar situation was suggested some time ago from ^{13}C-NMR investigations of Li/halide carbenoids $LiCH_2X$, $LiCHX_2$, $LiCX_3$ etc. by Seebach[25] and from calculations by von Ragué Schleyer[26]. This strongly suggests a *carbenoid nature* also for α-*oxygen*-substituted organolithium compounds[27]. ^{13}C-NMR investigations, IGLO calculations, and reactions with nucleophiles of α-oxygen-substituted organolithium compounds are in agreement with their Li/oxygen carbenoid nature[35].

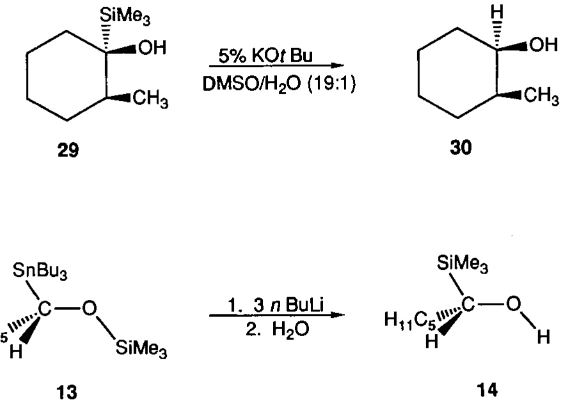
2.4. The Crystal Structure of 24 · 3THF and the Stereochemistry of the (Reverse) Brook Rearrangement

In the Brook rearrangement a silyl group migrates from a carbon to an oxygen atom; the other direction is observed in the reverse Brook rearrangement[36]. As outlined before, the remarkable aspect is the stereochemistry of the rearrangement: with *aryl* substituents at the carbon atom, *inversion* is observed (see Scheme 4). On the other hand, with *alkyl* groups at the carbon atom both rearrangements occur with *retention* (see Scheme 5).

Scheme 4. Brook (**27** → **28**[37]) and reverse Brook rearrangement (**15** → **16**[12]) with *aryl* groups at the carbon atom



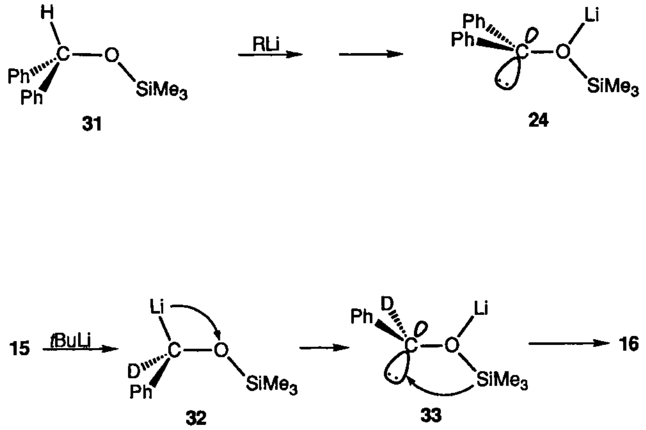
Scheme 5. Brook (**29** → **30**[38], followed by desilylation at the oxygen atom) and reverse Brook rearrangement (**13** → **14**[11]) with *alkyl* groups at the carbon atom



We propose a rationalization for the strongly substituent-dependent stereochemistry of these rearrangements by means of the following observations in the chemistry of α-oxygen-substituted organolithium compounds: (i) the retention of configuration in the deprotonation of ethers[6,8–10]; (ii) the retention of configuration in reactions of oxygen-substituted organolithium compounds with electrophiles if the anionic carbon atom is substituted with *alkyl* groups[6,10]; (iii) the crystal structure of **24** · 3THF (see section 2.3.); and (iv) the assumption that **24** · 3THF has a similar structure in solution as in the solid state; cryoscopic measurements with the crystalline **24** · 3THF in tetrahydrofuran at −108 °C do not disagree with this supposition: for concentrations between 99.08 mmol/kg and 272.65 mmol/kg **24** is monomeric under the conditions of the cryoscopic experiment.

The crystal structure of **24** · 3THF serves as a model for the *reverse Brook* rearrangement with *aryl* substituents at the carbon atom (**15** → **16**; Figure 3) if **24** · 3THF is formed from the diphenylmethyl trimethylsilyl ether **31** by deprotonation with retention of configuration, followed by suprafacial Li migration to the oxygen atom and inversion at the carbon atom (see also the discussion in section 2.2.).

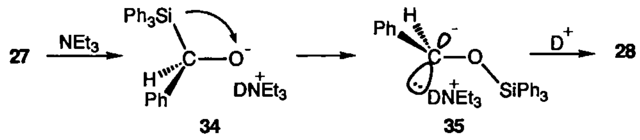
Scheme 6



A similar sequence in the case of **15** should first lead to **32** in which the negative charge at the carbon atom is likewise well-stabilized by a phenyl group. This allows migration of the lithium ion to the oxygen atom to give **33** with an *inverted* carbon atom – a situation observed in the crystal structure of **24** · 3 THF. **33** is all set for the intramolecular (experimentally found!) suprafacial migration of the trimethylsilyl group to give stereoselectively **16**.

An explanation for the *Brook* rearrangement with *aryl* groups at the carbon atom like the reaction **27**→**28** (Figure 3) deserves more caution because it involves in the final, stereochemistry-determining step **35**→**28** the deuteration of a silyloxy-substituted benzyl anion species.

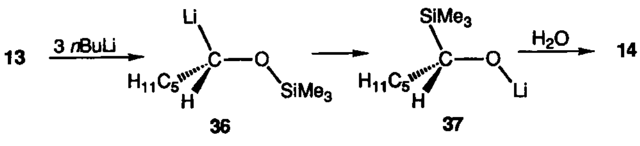
Scheme 7



The stereochemistry at least of carbamoyloxy-substituted benzyllithium compounds with electrophiles was found to be "capricious"[9]. Thus, the stereochemistry of the product **28** may not only depend on the stereochemistry of the intermediate ion pair **35** which is formed from **34**.

In the *Brook* and *reverse Brook* rearrangements with *alkyl* groups at the carbon atom (**29**→**30** and **13**→**14**, see Figure 4) configurationally rather stable metallated ethers[6,10] like **36** are involved.

Scheme 8



Since **36** is formed from **13** by tin-lithium exchange with retention of configuration[6], and since oxygen-substituted lithium compounds like **36** react with electrophiles with retention of configuration[6,10] it is not surprising that the trimethylsilylation **36**→**37**[39] also occurs with retention of configuration to give **14**. A rather similar situation (which therefore is not outlined in detail here) holds for the corresponding Brook rearrangement.

We are very grateful to the *Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 260*, and to the *Fonds der Chemischen Industrie* for supporting this work. A. O., and J. C. W. L. acknowledge a Graduierten-Stipendium of the *Graduierten-Kolleg "Metallorganische Chemie"* at the Fachbereich Chemie of the Universität of Marburg.

Experimental

Preparation of Diphenylmethyl Trimethylsilyl Ether (**31**): **31** was prepared according to Wright and West[40]. On the basis of IR- and NMR-spectroscopic data **31** corresponds in all aspects to the substance described in ref.[40].

Preparation of Single Crystals of $[Ph_2C(OSiMe_3)Li \cdot 3\,THF]$ (**24** · 3 THF): 0.34 g (1.33 mmol) of **31**, dissolved in 3 ml of THF/1 ml of hexane in the presence of 0.34 g (1.45 mmol, 1.1 mol equiv.) of (−)-sparteine was deprotonated with 1.46 mmol (1.1 mol equiv.) of *s*BuLi in cyclohexane at −78 °C. After careful removal of the solvents, the crystalline material, unsuitable for an X-ray structure investigation (too big, twinned), was washed with pentane and recrystallized from 0.2 ml of THF. Although not found in the crystals of **24** · 3 THF, (−)-sparteine is essential for the crystallization.

Determination of the Aggregation of $Ph_2C(OSiMe_3)Li$ (**24**) *in THF*: The determination of the aggregation *n* of **24** in THF was performed as described in ref.[41]. **24** was used in the form of crystalline **24** · 3 THF. The aggregation *n* was determined at five different concentrations. Independent of concentration **24** is monomeric in THF solution at −108 °C (see Table 5).

Table 5. Aggregation *n* of **24** in THF

Concentration of **24** · 3 THF [mmol/kg]	Aggregation *n*
94.08	1.00 ± 0.06
121.83	1.11 ± 0.10
135.37	1.09 ± 0.03
135.22	1.00 ± 0.02
272.65	1.22 ± 0.06

Crystal Structure Investigation of **24** · 3 THF: $C_{28}H_{43}LiO_4Si$ (478.7): An orange crystal with the dimensions 0.3 × 0.3 × 0.5 mm has been used for the data collection with an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Cu-K_α radiation.

Monoclinic space group *Cc* (Int. Tab. No. 9), lattice constants: a = 1530.0(3), b = 1013.0(2), c = 1936.9(4) pm; β = 109.60(3)°; V = 2828.0(10) × 10^6 pm^3; derived through centering of 25 reflections with $\Theta > 20°$; Z = 4, D(calcd.) = 1.124 g cm^{-3}; μ = 0.935 mm^{-1}; $F(000)$ = 1040. 4454 measured reflections; T = 193 ± 5 K, $2.0° \le \Theta \le 50°$, h (−15/15), k (−9/10), l (−19/19); ω scans; scan width (1.2 + 0.14 tg Θ)° ±25% for the background scans; 3 intensity control reflections every hour. After the Lp correction and merging of equivalent reflections there were 2815 unique reflections (R_{int} = 0.0389) and 2501 observed with $F_o \geq 4\sigma(F_o)$.

Structure solution with direct methods and full-matrix least-squares refinement have been performed with the Siemens SHELXTL PLUS (VMS) program system[42]. All non-hydrogen atoms have been refined anisotropically, hydrogen atoms "riding" with common isotropic temperature factors for different groups; extinction parameter X = 0.0027(2) {expression used: $F^* = F/[1 + 0.002 \times F^2/\sin(2\Theta)]^{0.25}$}; R = 0.0654; wR = 0.0537; 309 parameters. Quantum minimized: $\Sigma w(|F_o| - |F_c|)^2$; weighting scheme: $w = 1/\sigma^2(F_o)$. Mean "shift/error" 0.000 in the last refinement cycle; largest difference peak 0.49 e/Å^3. All calculations have been performed with a Micro-VAX II and a VAX 6000-420[43,44]. Atomic coordinates and equivalent isotropic displacement coefficients are found in Table 6.

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\times 10^{-1}$) (in pm^2) of **24** · 3 THF

	x	y	z	U(eq)
Si(1)	1126	295(2)	3501	51(1)
O(1)	2133(3)	-377(4)	3978(2)	39(2)
O(2)	4324(4)	-924(5)	5062(3)	57(2)
O(3)	3967(4)	791(5)	3666(3)	54(2)
O(4)	3535(4)	1877(5)	4998(3)	63(3)
C(1)	2127(5)	-1815(7)	4133(4)	45(4)
C(2)	2070(5)	-2084(8)	4818(4)	43(3)
C(3)	2111(7)	-3395(9)	5114(5)	76(5)
C(4)	2067(7)	-3628(10)	5775(5)	86(5)
C(5)	1946(7)	-2648(13)	6229(5)	94(6)
C(6)	1928(6)	-1378(10)	5961(5)	71(4)
C(7)	1986(5)	-1106(9)	5296(4)	52(4)
C(8)	2347(6)	-2589(7)	3591(4)	45(3)
C(9)	2685(6)	-2051(8)	3072(5)	58(4)
C(10)	2891(6)	-2774(9)	2554(4)	65(4)
C(11)	2804(6)	-4151(9)	2536(5)	65(4)
C(12)	2489(6)	-4687(8)	3040(5)	67(4)
C(13)	2255(6)	-4018(7)	3549(5)	61(4)
C(14)	1342(7)	2120(7)	3570(6)	101(6)
C(15)	184(5)	-119(8)	3860(5)	72(4)
C(16)	749(6)	-177(9)	2562(4)	86(4)
C(17)	4834(10)	-612(10)	5780(6)	168(8)
C(18)	5391(12)	-1834(15)	6114(8)	214(12)
C(19)	5430(9)	-2550(14)	5566(8)	146(7)
C(20)	4472(7)	-2313(9)	4976(7)	124(6)
C(21)	3551(6)	1567(8)	3026(4)	69(4)
C(22)	4127(8)	1437(12)	2555(6)	124(7)
C(23)	4761(7)	403(12)	2854(6)	112(6)
C(24)	4811(6)	215(12)	3619(5)	113(6)
C(25)	3286(8)	2127(11)	5626(5)	112(6)
C(26)	4001(11)	3043(12)	6073(7)	164(9)
C(27)	4307(7)	3799(10)	5569(5)	100(6)
C(28)	4143(7)	2919(9)	4905(5)	82(5)
Li(1)	3436(10)	233(12)	4412(6)	57(6)

Computational Methods: All geometries were calculated with the GAUSSIAN 90 program[45] and fully optimized in the given symmetry by using the 6-311 + + G(d,p)[46] basis set implemented in the program and second-order Moeller-Plesset pertubation theory[47]. Stationary points were identified by frequency analysis; minima had no, the planar configurations in Table 2 exactly one imaginary frequency. Energies in Table 3 were corrected to zero-point vibration based on Hartree-Fock 6-311 + + G(d,p) frequencies on the MP2/6-311 + + G(d,p) geometries.

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* Dedicated to Professor *Günther Maier* on the occasion of his 60th birthday.

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