α-Oxygen-Substituted Organolithium Compounds and their Carbenoid Nature: Reactions with RLi and Other Nucleophiles, Experimental and IGLO-Calculated ^{13}C-NMR Shifts of the Carbenoid C Atom☆

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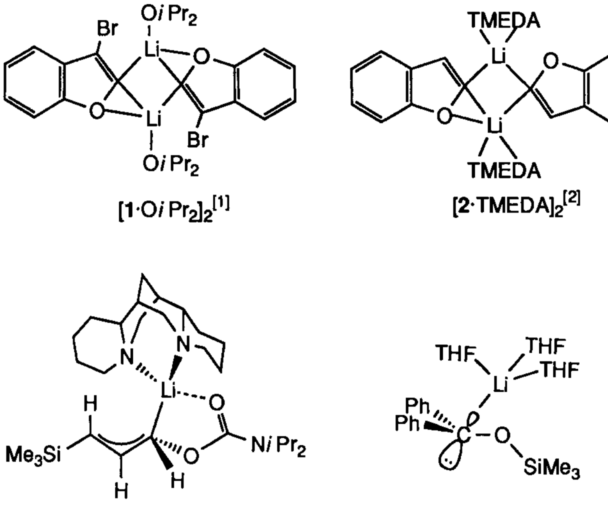
In addition to the earlier[1] demonstrated C—O bond elongation between the anionic carbon atom and oxygen in α-lithiated ethers which indicates a carbenoid character of these compounds we provide further evidence for this property in this publication. Thus, α-lithiated ethers RCH(Li)—OR′ react as electrophiles with nucleophiles R″Li to give RCH(Li)—R″ + LiOR′, and the ^{13}C-NMR signal of the carbenoid C atom is shifted downfield (compared to the ^{13}C signal of the corresponding non-lithiated compound). Since the latter two observations are also made in the Li/*Hal* carbenoid series, α-lithiated ethers indeed are Li/oxygen carbenoids. Furthermore, for the first time we have calculated the ^{13}C shifts of carbenoid C atoms in the Li/oxygen carbenoid series by means of the IGLO method: the calculated data agree nicely with the experimental ones. They even allow the preferred bridged structure in solution to be determined.

In a recent publication[1] we have shown that the C—O bond lengths between the anionic carbon atoms and the oxygen atoms in the α-lithiated ethers $[\mathbf{1} \cdot \mathrm{O}i\mathrm{Pr}_2]_2$, $[\mathbf{2} \cdot \mathrm{TMEDA}]_2$[2], **3** · sparteine, and **4** · 3 THF are remarkably *elongated* (7—10 pm) as compared to the C—O bond lengths in the corresponding non-lithiated species.



$[\mathbf{1}\cdot\mathrm{O}i\mathrm{Pr}_2]_2$[1] $[\mathbf{2}\cdot\mathrm{TMEDA}]_2$[2]

3·sparteine[1] **4**·3THF[1]

Figure 1. α-Lithiated ethers with known crystal structures

This is exactly what has been suggested from ^{13}C-NMR investigations of Li/*halide* carbenoids by Seebach et al.[3] for the C—Hal bonds in these species. Theoretical investigations mainly by Schleyer et al.[4] on Li/*halide* carbenoids have confirmed the conclusions drawn from the NMR results. Since model calculations of $LiCH_2OH$ have also predicted a *lengthening* of the C—O bond as compared to the C—O bond in CH_3OH[5,4h,1] it is strongly suggestive that the α-lithiated ethers shown in Figure 1 reveal structures typical of *Li/oxygen carbenoids*, and thus for the first time crystal structures of carbenoids[1,6].

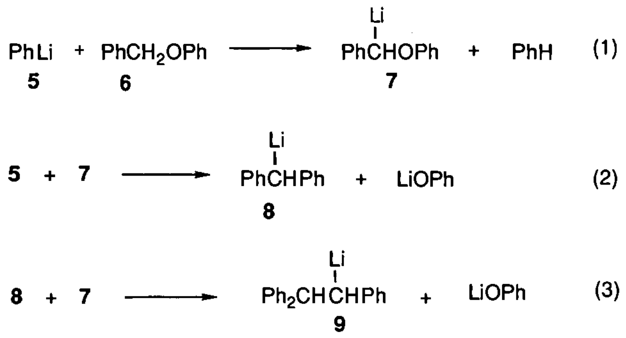
In this paper we confirm the *Li/oxygen carbenoid* nature of α-lithiated ethers by means of reactions which are typical of carbenoids[7], and by investigations of the ^{13}C-chemical shifts (and ^{6}Li/^{13}C coupling constants) of the lithiated carbon atoms which support the above mentioned results. Furthermore, we demonstrate for the first time the successful application of the IGLO method to the calculation of the ^{13}C-chemical shifts of (Li/oxygen) carbenoid carbon atoms.

1. Reactions of α-Lithiated Ethers with Nucleophiles RLi, Olefines, C—H Bonds, and their Fritsch-Buttenberg-Wiechell Rearrangement

In order to cover the full range of reactions of α-lithiated ethers which characterize them as *Li/oxygen carbenoids* we present our own investigations together with results from the literature which so far have not been summarized under this particular aspect.

The first carbenoid reaction of an α-lithiated ether has been described by Lüttringhaus and Sääf in a publication revealing α-lithiated ethers probably for the first time[8a]. These authors have treated phenyllithium (**5**) (1.3 mol. equiv.) with benzyl phenyl ether (**6**) in diethyl ether at 45°C for 1.5 hours leading first to α-lithiated benzyl phenyl ether (**7**) and benzene in a deprotonation reaction, see Scheme 1, reaction (1).

Scheme 1. Reaction of phenyllithium (**5**) with benzyl phenyl ether (**6**) and consecutive reactions[8a]



$$\underset{\mathbf{5}}{PhLi} + \underset{\mathbf{6}}{PhCH_2OPh} \longrightarrow \underset{\mathbf{7}}{Ph\overset{Li}{C}HOPh} + PhH \qquad (1)$$

$$\mathbf{5} + \mathbf{7} \longrightarrow \underset{\mathbf{8}}{Ph\overset{Li}{C}HPh} + LiOPh \qquad (2)$$

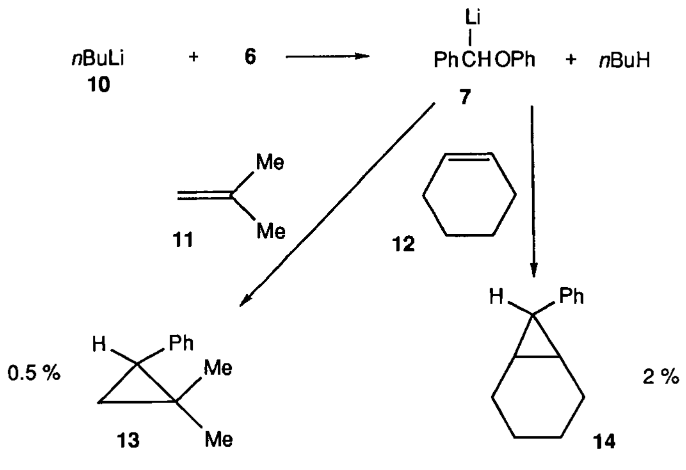
$$\mathbf{8} + \mathbf{7} \longrightarrow \underset{\mathbf{9}}{Ph_2CH\overset{Li}{C}HPh} + LiOPh \qquad (3)$$

However, the reaction does not stop at that stage: phenyllithium not only reacts with the ether **6** but also with *α-lithiated benzyl phenyl ether* (**7**) to give diphenylmethyllithium (**8**) and lithium phenoxide (Scheme 1, reaction 2). Here, phenyllithium acts as a nucleophile, and the *"anion"* **7** as an *electrophile.* Not surprisingly, in a further reaction of this type (reaction 3), **8** reacts also with **7** to give **9** and lithium phenoxide. On protonation **8** forms diphenylmethane (14%), and **9** gives 1,1,2-triphenylethane (33%). Thus, the lithiated ether **7** behaved clearly as a *Li/oxygen carbenoid.*

Wittig and Löhmann[9] have confirmed these results and noticed a "higher mobility" of the phenolate group in the lithiated ether **7** as compared to the normal ether **6**.

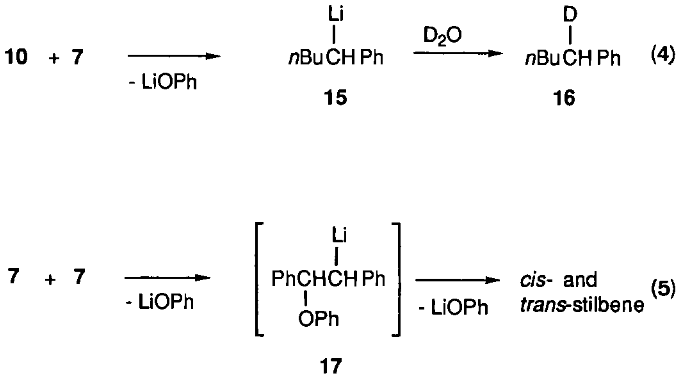
In a further investigation with **7**, Schöllkopf and Eisert[10] have used *olefins* as nucleophiles and obtained the cyclopropanes **13** and **14** albeit in low yields (Scheme 2). Ether **7** is prepared from ether **6** by means of the base *n*-butyllithium (**10**, 1.1 mol. equiv.) in diethyl ether in the presence of isobutene (**11**); the reaction is performed at 25°C for 14 days. The cyclohexene (**12**) reaction takes "only" 10 hours at 0–35°C and overnight at room temperature.

Scheme 2. Reaction of the carbenoid **7** with olefins leading to cyclopropanes[10]



The formation of the cyclopropanes **13** and **14** from the lithiated ether **7** and the respective olefins also proves the carbenoid nature of **7**[7]. The low yields of **13** and **14** are at least in part due to facile side reactions of **7** with *n*-BuLi (**10**) and consecutive products thereof (compare Scheme 1). Thus, the formation of the substitution product **15** from *n*BuLi (**10**) and carbenoid **7** has been proven by deuteration to give **16**, Scheme 3, reaction (4).

Scheme 3. "Side reactions" of the carbenoid **7**[10]

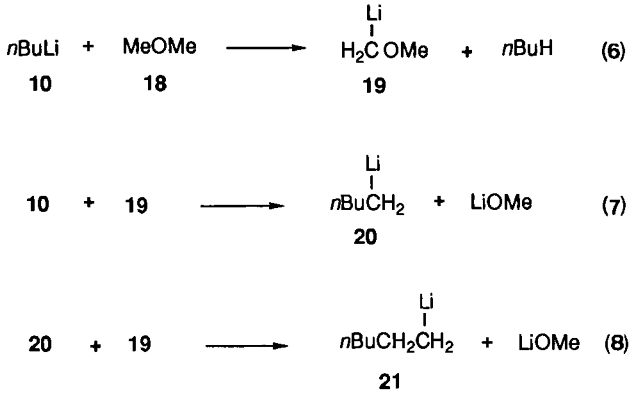


$$\mathbf{10} + \mathbf{7} \xrightarrow[-\,LiOPh]{} \underset{\mathbf{15}}{nBu\overset{Li}{C}HPh} \xrightarrow{D_2O} \underset{\mathbf{16}}{nBu\overset{D}{C}HPh} \qquad (4)$$

$$\mathbf{7} + \mathbf{7} \xrightarrow[-\,LiOPh]{} \underset{\mathbf{17}}{\left[Ph\overset{Li}{C}H\underset{OPh}{C}HPh\right]} \xrightarrow[-\,LiOPh]{} \textit{cis- and trans-}\text{stilbene} \qquad (5)$$

Furthermore, the Li/oxygen carbenoid **7** reacts both as a *nucleophile* and an *electrophile* to give the intermediate **17** which after fast elimination of lithium phenoxide affords *cis-* and *trans*-stilbene[10], Scheme 3, reaction (5).

Scheme 4. Cleavage of dimethyl ether (**18**) with *n*-butyllithium in a deprotonation (reaction 6) – substitution sequence (reactions 7, 8)[11]



$$\underset{\mathbf{10}}{nBuLi} + \underset{\mathbf{18}}{MeOMe} \longrightarrow \underset{\mathbf{19}}{H_2\overset{Li}{C}OMe} + nBuH \qquad (6)$$

$$\mathbf{10} + \mathbf{19} \longrightarrow \underset{\mathbf{20}}{nBu\overset{Li}{C}H_2} + LiOMe \qquad (7)$$

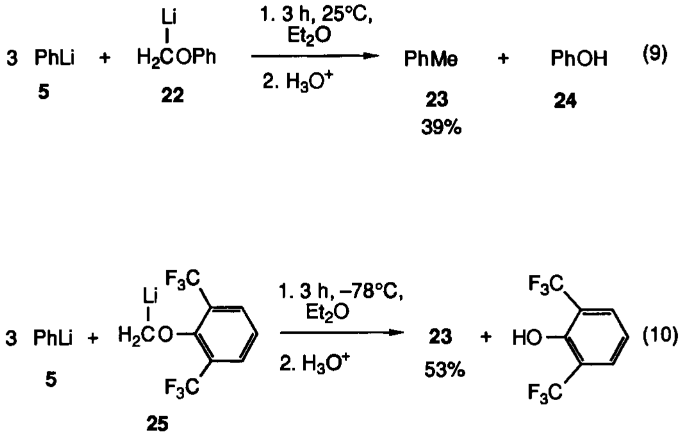
$$\mathbf{20} + \mathbf{19} \longrightarrow \underset{\mathbf{21}}{nBuCH_2\overset{Li}{C}H_2} + LiOMe \qquad (8)$$

The "ether cleavage reaction" of the α-lithiated ether **7** by the organolithium compounds phenyllithium (**5**), diphenylmethyllithium (**8**), or *n*-butyllithium (**10**) is not limited to *activated* Li/oxygen carbenoids like **7** (the nucleophilic substitution takes place in a *benzylic* position; lithium *phenoxide* is a more efficient leaving group than lithium *alkoxide*). Ziegler and Gellert[11] have discovered that dimethyl ether (**18**) is cleaved by organolithium reagents like *n*-butyllithium (**10**) in a similar α-lithiation-substitution sequence, although *much slower*: the reaction has been allowed to run for 7 days at 40°C (Scheme 4).

The carbenoid **19**, formed according to equation (6), reacts in a second step with *n*-butyllithium to give lithium methoxide and *n*-pentyllithium (**20**) (reaction 7), which also reacted with **19** (reaction 8) to give **21** and finally a homologous series of hydrocarbons after protonation. Hoberg[12] has been able to trap the carbenoid $LiCH_2OnBu$ with cyclohexene as norcarane (characterized by IR and GC; the very low yield has not been determined exactly) after treatment of *n*-butyl methyl ether with 0.4 mol. equiv. of *n*BuLi in the presence of cyclohexene for 100 hours at 55°C. Systematic investigations of dialkyl ether "cleavage reactions", which also include Li/oxygen carbenoid reactions with RLi as shown above have been performed by Maercker[13].

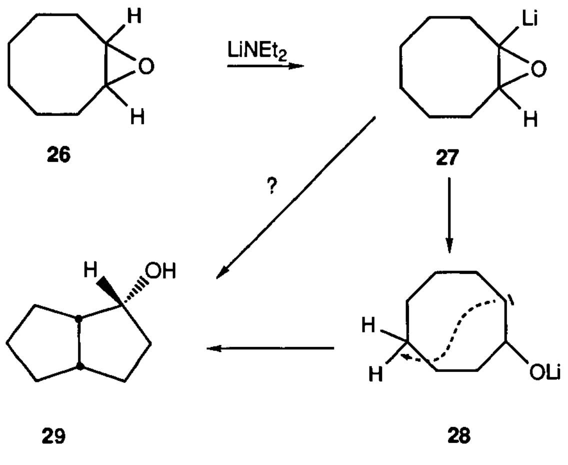
The reaction of the lithiated methyl phenyl ether **22** (prepared from the corresponding tributyltin compound) with 3 mol. equiv. of phenyllithium (**5**) in diethyl ether for 3 hours at 25°C, results in the formation of toluene (**23**, 39%) and phenol (**24**, 94%) isolated on protonation (Scheme 5, reaction 9).

Scheme 5. The importance of the leaving group in Li/O carbenoid reactions with phenyllithium (**5**)



The reaction of the related bis(trifluoromethyl)phenyl-substituted carbenoid **25** with phenyllithium (**5**) leads to toluene (**23**) in 53% yield even at *–78°C* (reaction 10) which clearly emphasizes the importance of the leaving group in such reactions.

Scheme 6. Insertion of the carbenoid **27** [carbene **28** (?)] into a C–H bond[14]

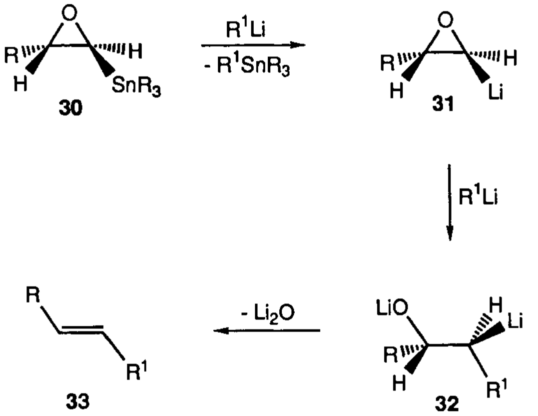


This latter aspect is nicely corroborated by the chemistry of α-lithiated oxiranes in which case the α-elimination to a carbene as well as the nucleophilic substitution reaction take advantage of the loss of strain in the three-membered ring. The Li/oxygen carbenoid nature of these compounds has first been demonstrated by Cope et al.[14] The reaction of the oxirane **26** with bases like lithium diethylamide first leads to the α-lithiated oxirane **27**, which subsequently reacts with a *C–H* bond across the ring to give the bicyclic alcohol **29**, see Scheme 6.

Cope et al. have surmised the carbene **28** to insert into the C–H bond. The reaction of the carbenoid **27**, however, has not been excluded.

The high reactivity of lithiated oxiranes has been widely utilized in synthesis[15–20] as, e.g., in the "reductive alkylation", discovered by Crandall[15], see Scheme 7.

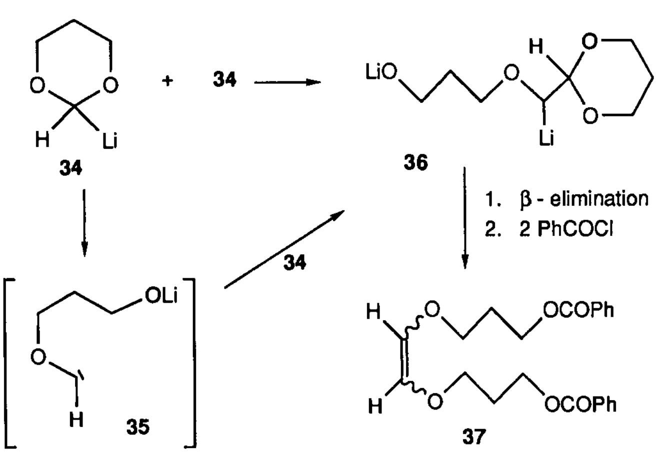
Scheme 7. "Reductive alkylation"[15] of α-lithiated oxiranes with formation of olefins



The reaction of the lithiated oxirane **31**, as e.g. prepared from the tin compound **30**, with an organolithium species R^1Li leads to **32** which with the elimination of Li_2O is converted to the olefin **33**.

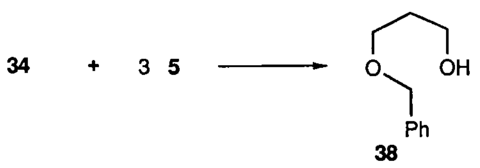
The question whether it is the carbenoid or the carbene which reacts with the nucleophile is also not settled for a reaction recently discovered by Shiner et al.[21], namely the thermal decomposition of the *di*alkoxymethyllithium species **34**, see Scheme 8.

Scheme 8. Thermal "decomposition" of the carbenoid **34** leading to the olefin **37**[21]



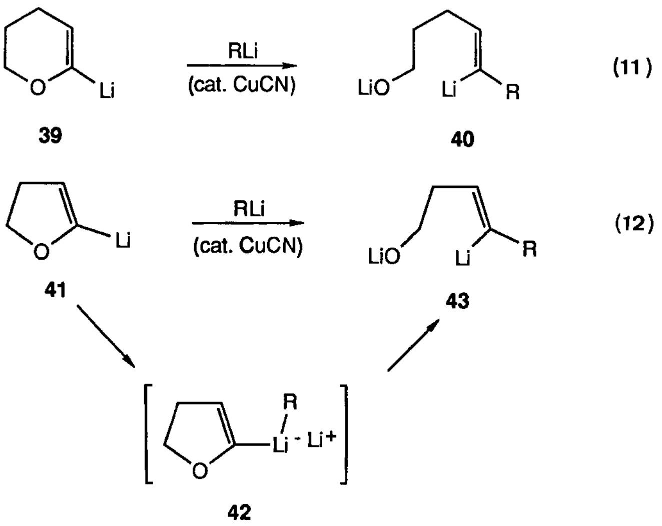
Warming a solution of **34** in THF to room temperature followed by reaction with benzoyl chloride yields a 1:1 mixture of the (*E*)- and (*Z*)-dibenzoates **37**. Intermediate **36** (which after β-elimination and reaction with benzoyl chloride is converted to **37**) could have resulted either from a reaction of the "*nucleophile* **34**" with the "*carbenoid* **34**" ("dimerization"), or with the carbene **35**. In our experiment, the carbenoid **34** reacts with 3 mol. equiv. of phenyllithium (**5**) to give the substitution product **38** even at −78 °C, see Scheme 9.

Scheme 9. Reaction of the carbenoid **34** with phenyllithium (**5**)



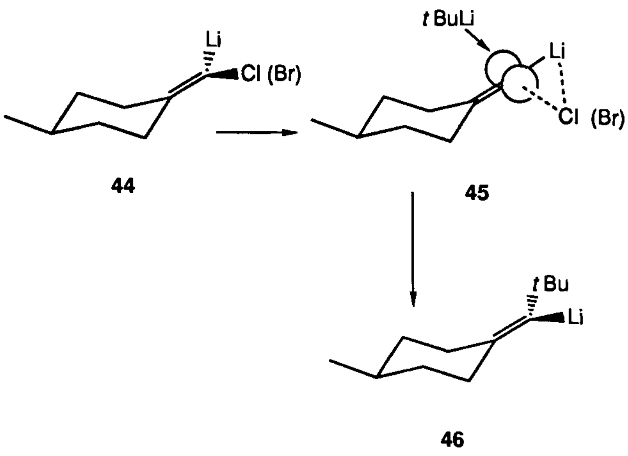
More surprisingly, carbenoid reactivity towards nucleophiles RLi is also observed in the case of α-lithiated *cyclic unsaturated ethers*[22], that is at an sp^2-hybridized carbon atom. Kocieński[23] has summarized the reactions of the lithiated dihydropyran **39** and especially dihydrofuran **41** which give the substitution products **40** and **43**, respectively, with inversion of configuration, see Scheme 10, reactions 11 and 12. It should be mentioned that the CuCN-catalyzed reactions are synthetically more useful[23].

Scheme 10. Reaction of α-lithiated cyclic unsaturated ethers with nucleophiles[23]



The incoming RLi is assumed to form first an ate complex of the type **42** which undergoes an *intra*molecular 1,2-migration of R with inversion of configuration at the carbenoid carbon atom[23]. Some years earlier Duraisamy and Walborsky have found a comparable substitution reaction with *t*BuLi to occur at the noncyclic vinylic Li/Cl(Br) carbenoid **44** which likewise proceeds with inversion of configuration to give **46**[24], see Scheme 11.

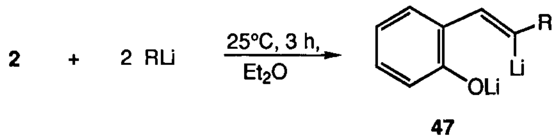
Scheme 11. "Metal-assisted ionization"[24] in the substitution reaction of the carbenoid **44** with *t*BuLi



The authors have proposed a "normal" substitution reaction (which, of course, does not occur at a non-metalated sp^2 carbon atom!) made possible here by "metal-assisted ionization" (**45**). A similar explanation for the reactions of Li/Hal carbenoids with nucleophiles has been given by Köbrich[7b]. Metal-assisted ionization of the ether bond similarly facilitates reactions of *Li/O* carbenoids with nucleophiles.

An interesting question with regard to the carbenoid nature of α-lithiated ethers is whether [**1** · O*i*Pr$_2$]$_2$, [**2** · TMEDA]$_2$[2], **3** · sparteine, and **4** · 3 THF, which according to X-ray structure determinations are characterized by elongated C—O bonds at the anionic C atom (see the introduction), also react with nucleophiles RLi. The first compound which we have investigated is the lithiated benzofuran **2**, see Scheme 12.

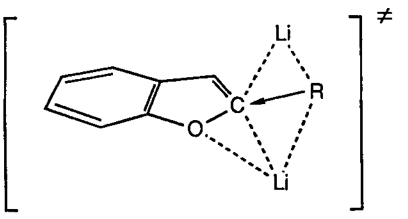
Scheme 12. Reactions of α-lithiobenzofuran (**2**) with RLi to give the substitution products **47**, isolated after protonation; in parentheses the results of Nguyen and Negishi[25] are given



R	yields [%] of **47**
Me	38 (not reported)
*n*Bu	64 (90)
*s*Bu	- (78)
*t*Bu	- (92)
Ph	42 (almost 100)

Compound **2** is prepared by deprotonation of benzofuran with *n*Bu-Li/TMEDA (TMEDA = tetramethylethylenediamine) in ether for 30 min at room temperature. Then it is allowed to react with 2 mol equiv. of RLi for 3 hours at room temperature, and the mixture was worked up with H_2O. The reaction occurs with CH_3Li, *n*BuLi, and PhLi. In contrast to Nguyen and Negishi who have studied the same reaction independently we have not been able to isolate the reaction products in the cases of *s*BuLi and *t*BuLi[25].

The strongly lengthened C1–O1 bond in the dimer [**2** · TMEDA]$_2$[2] (as well as in the related dimer [**1** · O*i*Pr$_2$]$_2$) are in good agreement with these substitution reactions: the σ_{C-O} bond is weakened and thus more easily attacked (lower σ^* orbital!) by a nucleophile[26]. Furthermore, if the bridging of the C1–O1 bond by Li, and the dimer formation as observed in the solid state, also prevail in solution, which is in agreement with ^{13}C-NMR investigations in the solution of [**2** · TMEDA]$_2$[2] (see section 2) as well as with calculated structures[1,27], one can deduce the following model $\mathbf{48}^{\neq}$ for the transition state of this substitution reaction, see Figure 2.



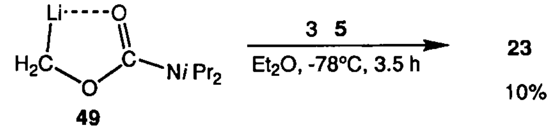
$\mathbf{48}^{\neq}$

Figure 2. Transition state model $\mathbf{48}^{\neq}$ of the reactions of the Li/oxygen carbenoid **2** with RLi

The nucleophile RLi forms a *mixed* complex with the Li-bridged carbenoid – note that this structure is rather similar to the solid-state *dimer* structures of [**2** · TMEDA]$_2$ and [**1** · O*i*Pr$_2$]$_2$, and also to a Li–ate complex – which places R in a position to attack the elongated C–O bond from the backside. Thereby the bridging Li helps to cleave the C–O bond ("metal-assisted ionization"[24,7b]). One can envisage a similar transition state for the reactions of "normal" α-lithiated dialkyl ethers with RLi.

Although in compounds like the carbamoyloxy-substituted **3** · sparteine[28] in the solid state Li does not bridge the adjacent oxygen atom (see introduction), Li is likewise attached to the carbenoid carbon atom *and* the leaving group, here by five-membered ring chelation, a structural type which is also observed in solution (see Section 2). It is thus not surprising that the lithiated carbamoyloxy species **49** also reacts with a nucleophile RLi, namely phenyllithium (**5**), to give toluene (**23**) in 10% yield, see Scheme 13.

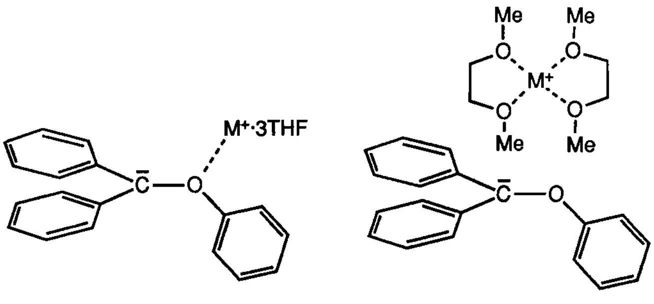
Scheme 13. Reaction of the lithiated carbamoyloxy species **49** with phenyllithium (**5**)



A transition state analogous to $\mathbf{48}^{\neq}$ (Figure 2) is in agreement with this result.

A totally different observation has been made with **4** · 3 THF (see introduction), a structural Li/oxygen carbenoid isomer in which lithium is not bound to the anionic carbon atom. Rather, it is only coordinated to the ether oxygen of **4** and to three THF molecules. Such a structure seems also to exist in solution. This is derived from a comparison of UV/Vis absorption spectra of fluorenyl-alkali metal species[29] with those of phenoxydiphenylmethyl-Li(Na, K) compounds[30,31], see Scheme 14.

Scheme 14. UV/Visible absorption bands of phenoxydiphenylmethylakali metal compounds (M = Li, Na, K) in THF (**50**) and glyme (**51**), respectively[30,31]

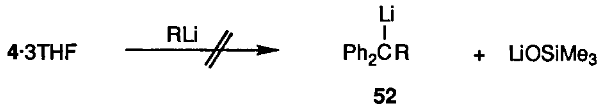


50, λ_{max} = 450 nm
contact ion pairs

51, λ_{max} = 460 nm
solvent-separated ion pairs

In contrast to the absorption band of contact ion pairs like those of fluorenylalkali metal compounds which depends on the counterion (Li$^+$ 349 nm; Na$^+$ 356 nm; K$^+$ 362 nm; Cs$^+$: 364 nm), this is not so in the case of **50**: in THF, the Li$^+$, Na$^+$, and K$^+$ species absorb at 450 nm. Consequently, the counterion cannot be bound to the anionic *carbon* atom(s) of the diphenylmethyl part of **50**. The solvent-separated ion pair **51**, which is formed in glyme, absorbs at 460 nm. A similar situation as for **50** in THF should hold for the silyl compound **4** in THF. Moreover, **4** · 3 THF is a *monomer* in THF at –108°C[1].

Attempts to react **4** · 3 THF in THF (as well as in diethyl ether and hydrocarbon solvents) with RLi *nucelophiles* to obtain the expected reaction product **52** have failed.

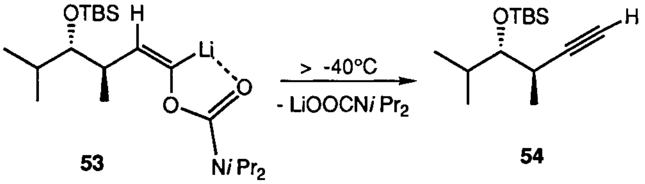


$$\mathbf{4}\cdot 3\mathrm{THF} \xrightarrow[\not\;]{\mathrm{RLi}} \underset{\mathbf{52}}{\overset{\mathrm{Li}}{\mathrm{Ph_2CR}}} + \mathrm{LiOSiMe_3}$$

The reactions have been performed like the others mentioned in this chapter which indeed afford substitution products of Li/oxygen carbenoids with RLi. For details of the reactions of **4** · 3 THF with RLi see Experimental. Although we do not have a definitive explanation for this behavior it seems that it is the *ylide* nature of **4** which forbids an attack of nucleophiles like RLi at the anionic, not lithium-bound carbon atom.

In summary, α-lithiated ethers (except for **4**) react as expected from the elongated C–O bonds like Li/oxygen carbenoids: RLi substitutes LiOR; they add to C=C bonds to give cyclopropanes; they insert into C–H bonds, and finally they undergo the Fritsch-Buttenberg-Wiechell rearrangement as demonstrated by the formation of **54** from **53**[23a], see Scheme 15.

Scheme 15. Fritsch-Buttenberg-Wiechell rearrangement of the carbenoid **53** with formation of the acetylene **54**[23a]



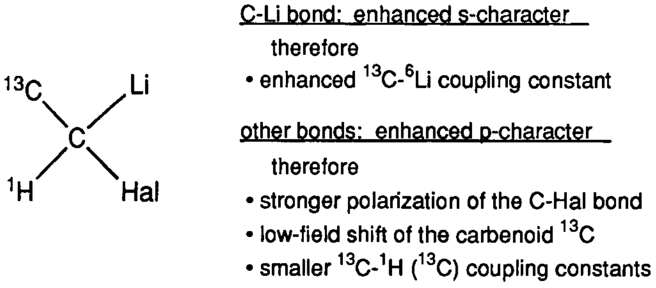
It should be mentioned that the leaving group in this reaction is the same as in the case of the substitution reaction of **49** (see Scheme 13).

The following ^{13}C-NMR investigations of α-lithiated ethers confirm their Li/oxygen carbenoid nature and preferred bridged structure.

2. ^{13}C-NMR Investigations and IGLO Calculations

The first NMR investigations of Li/*halogen* carbenoids have been performed by Seebach et al.[3] A brief summary of their results is shown in Scheme 16.

Scheme 16. Conclusions based on NMR studies of Li/Hal carbenoids[3]

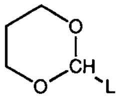
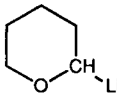
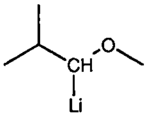
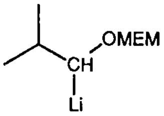
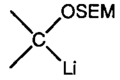
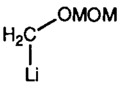
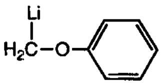
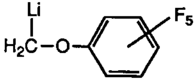
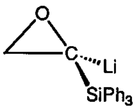
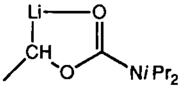
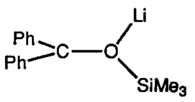
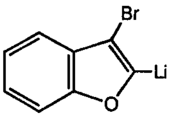
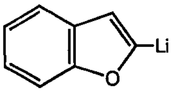


Most significantly, the signal of the carbenoid ^{13}C atom is markedly shifted downfield compared to that of the non-lithiated precursor. In Table 1 are listed our NMR data of α-lithiated ethers together with some earlier data.

The downfield shift of the carbenoid ^{13}C atom in $LiCCl_3$ (**55**) ($\Delta\delta = 65.9$) and $LiCHCl_2$ (**56**) (50.0) clearly shows the influence of the number of halogen atoms which is in agreement with $LiCH_2Cl$ (**57**) ($\Delta\delta = 32.3$). Most importantly with respect to the carbenoid nature of α-lithiated ethers, these compounds similarly show a remarkable downfield shift: in **34** with two oxygen substituents at carbon the shift is more pronounced ($\Delta\delta = 40.0$) than in **58** (26.2), **59** (26.4), **60** (27.8), **61** (28.0), **62** (19.0), **22** (19.7), **63** (29.9), and **64** (36.9)[34]. The chelate dipole-stabilized **65** shows a much smaller shift ($\Delta\delta = 7.0$) while the lithiated ether **4** with Li only bound to oxygen has even a slightly smaller downfield shift Δδ (34.8) than the model system diphenylmethane → diphenylmethyllithium (38.7)[3d]. In **4** and diphenylmethyllithium the downfield shift is due to rehybridization at the anionic carbon atom; an additional "carbenoid" shift is thus not observed for **4**.

It is interesting to compare the Δδ value of lithiated methyl *phenyl* ether (**22**, 19.7) with that of lithiated methyl

Table 1. δ values [ppm] of the carbenoids listed; measurements in [D$_8$]THF and/or 2-methyltetrahydrofuran between −80 and −120°C; Δδ refers to the corresponding non-lithiated compounds

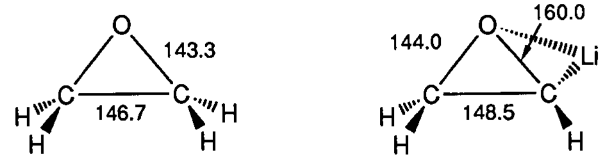
	Carbenoid	δ	Δδ	^1J (^{13}C,^{6}Li) [Hz]
55[a]	$LiCCl_3$	145.9	65.9	17.0 (t)
56[a]	$LiCHCl_2$	105.5	50.0	16.3 (t)
57	$LiCH_2Cl$	57.9	32.3	(sb)
34		134.8	40.0	(sb)
58		95.7	26.2	(sb)
59		106.4	26.4	6.8 (quint)
60[b]		102.4	27.8	(sb)
61[c]		96.7	28.0	(svb)
62[d,e]		74.0	19.0	(sb)
22		74.5	19.7	(sb)
63		92.2	29.9	(sb)
64[f]		79.0	36.9	(sb)
65[g]		67.3	7.0	14.4 (t)
4[h]		111.2	34.8	(sb)
1[i]		218.4	73.7	13.9 (t)
2[j,k]		215.6	70.8	7.7 (quint)

[a] Determined by Seebach et al.[3] – [b] MEM = (2-methoxyethoxy)methyl. – [c] SEM = [2-(trimethylsilyl)ethoxy]methyl. – [d] See ref.[32]. – [e] MOM = methoxymethyl. – [f] In [D$_8$]THF/TMEDA. – [g] In [D$_{10}$]diethyl ether. – [h] See ref.[1a]. – [i] See ref.[33]. – [j] Determined by Harder et al.[2]. – [k] In toluene/TMEDA. sb = broad singlet; svb = very broad singlet.

pentafluorophenyl ether (**63**, 29.9): **63** which has a more efficient leaving group (pentafluorophenolate instead of phenolate) exhibits a more pronounced downfield shift. This is in agreement with the results shown in Scheme 5.

The ^{13}C-NMR shift of the lithiated oxirane **64** confirms these results: the Δδ value of 36.9 is even higher than that of $LiCH_2Cl$ (32.3)![34] It thus seems that the high reactivity of lithiated oxiranes as outlined in Section 1 is related to the extraordinary downfield shift of the carbenoid C atom. A MP2/6-311++G(d,p)//MP2/6-311++G(d,p) calculation of oxirane **66** and lithiated oxirane **67** shows the strong elongation of the carbenoid C–O bond, see Scheme 17.

Scheme 17. Calculated [MP2/6-311++G(d,p)] bond lengths [pm] of oxirane **66** and lithiated oxirane **67**

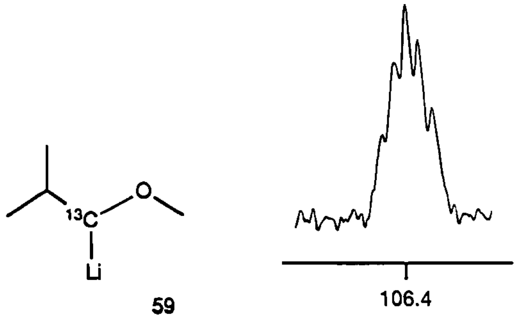


66 **67**

The lacking downfield shift of the signal of the anionic carbon atom of **4** seems to fit into this shift pattern: as pointed out in Section 1, substitution reactions of **4** with RLi are unknown to date.

For the vinylic carbenoids **1** and **2** large Δδ values are obtained, i.e. 73.7 and 70.8, respectively. This is a general phenomenon of lithiated sp^2 carbon atoms. For example, monomeric phenyllithium has a Δδ value of 68.1[35], while it is 60.3 for the dimer[3d]; the signal for the vinyllithium tetramer is shifted by 54.4[36]. However, a comparison of the results of **1** and **2** with those of phenyllithium and vinyllithium shows that the former compounds have slightly larger Δδ values, thus again confirming their Li/oxygen carbenoid nature.

In the ^{13}C-NMR spectrum of ^6Li-isobutyl methyl ether (**59**) the ^{13}C signal in solution appears as a *quintuplet*, see Table 1 and Figure 3. Similarly, a ^{13}C *quintuplet* had been found in the case of **2**[2].

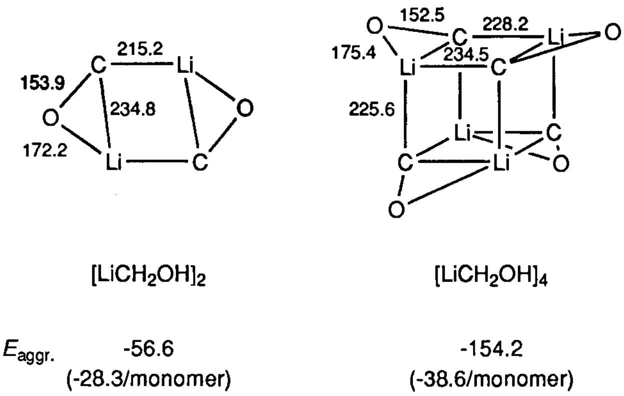


59

Figure 3. The ^{13}C-NMR signal (δ scale) of the carbenoid C atom of **59**

This splitting pattern results from the coupling of *two* ^6Li atoms with the carbenoid ^{13}C atom. Consequently, under the conditions of the NMR experiment **59** and **2** cannot be *monomers*. Indeed, MP2/6-31G(d)//3-21G calculations of the bridged *dimer* and *tetramer* of $LiCH_2OH$ show clearly how advantageous aggregation is, see Scheme 18.

Scheme 18. The dimer and tetramer of $LiCH_2OH$ [MP2/6-31G(d)//3-21G calculations]; energies [kcal/mol]; bond lengths [pm]; hydrogens omitted

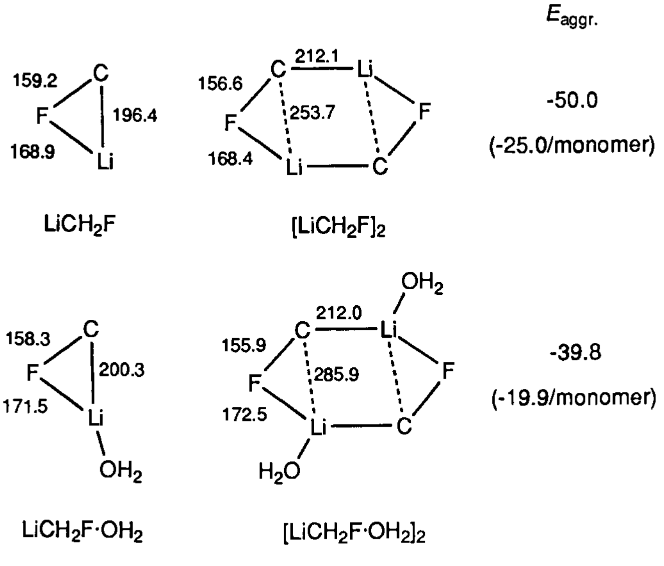


In the bridged dimer $[LiCH_2OH]_2$ two ^6Li are bound to one ^{13}C. As indicated earlier and as extensively outlined in ref.[1] the bridged structure is the most favorable one.

The solid-state structures of [**1** · O*i*Pr_2]$_2$ and [**2** · TMEDA]$_2$ emphasize this clearly[37]. They even show the favorable dimer formation. The $^6Li^{13}C$ quintuplets observed in the ^{13}C-NMR spectra of **59** and **2** therefore clearly indicate bridged dimers in solution, too[38]. In the tetramer $[LiCH_2OH]_4$ each carbon is coordinated to three Li atoms.

The above findings are different from earlier observations in the ^{13}C-NMR spectra of $^6Li^{13}CCl_3$ (**55**) and $^6Li^{13}CHCl_2$ (**56**) in which cases a ^{13}C *triplet* has been observed[3d]. Are these C/Hal carbenoids monomers? By calculating [MP2/6-31G(d)//3-21G] a dimeric structure of the Li/Hal model carbenoid $LiCH_2F$, we have found a stable bridged dimer

Scheme 19. MP2/6-31G(d)//3-21G energies [kcal/mol] and bond lengths [pm] of bridged $LiCH_2F$, $LiCH_2F \cdot OH_2$, $[LiCH_2F]_2$, and $[LiCH_2F \cdot OH_2]_2$; hydrogens omitted

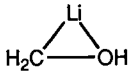
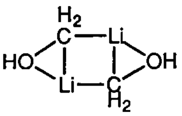
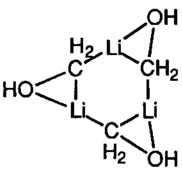
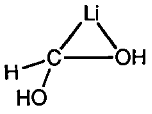
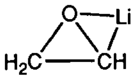
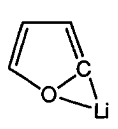
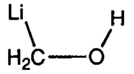


$[LiCH_2F]_2$ which is structurally *related* to $[LiCH_2OH]_2$, compare Schemes 18 and 19[39].

A remarkable *difference* between $[LiCH_2OH]_2$ and $[LiCH_2F]_2$ exists, however, in the longer distance of the bridging Li to C (253.7 pm) in the latter compound as compared to $[LiCH_2OH]_2$ (234.8 pm). Solvation of Li increases this distance, as shown by the structure of $[LiCH_2F \cdot OH_2]_2$ (285.9 pm). This implies that Li/Hal carbenoids might still be aggregated (e.g. to dimers). However, only *one* ^6Li-^{13}C coupling is observed because of the large distance of the bridging ^6Li to the carbenoid ^{13}C atom.

The intriguing *downfield* ^{13}C chemical shifts of Li/Hal[3] and Li/oxygen carbenoids (Table 1) raise the question whether they are in accord with a theoretical model. In order to check this we have used the IGLO (Individual Gauge for Localized Orbitals) method developed by Kutzelnigg and Schindler[40]. This method is very helpful in determining the structures of carbocations[41]. Very recently, it has been applied to organolithium compounds[42]. Our calculations of carbenoids are the first of such species. The results are listed in Table 2.

Table 2. IGLO calculations of Li/oxygen carbenoids

Carbenoid	$\Delta\delta$ [a]	Opt. geometry
	29.7	MP2/6-311++g(d,p)
	34.4	3-21G
	27.6	3-21G
	43.3	6-311++g(d,p)
	54.8	MP2/6-311++G(d,p)
	76.8	6-31G(d)
	6.3	MP2/6-311++G(d,p)

[a] $\Delta\delta$ refers to the corresponding protonated compound; basis sets: IGLO II+sp except for entries 2 and 3 (IGLO DZ+sp).

The calculated IGLO values of the *bridged* $LiCH_2OH$ monomer, dimer, and trimer in Table 2 agree nicely with the experimental results of **58**, **59**, **60**, **61**, **62**, **22**, and **63** (Table 1). The bridged dihydroxylated model $LiCH(OH)_2$ ($\Delta\delta$ = 43.3) comes close to the lithiated acetal **34** ($\Delta\delta$ = 40.0). The comparatively large shift as observed in the case of the lithiated triphenylsilyl-substituted oxirane **64** ($\Delta\delta$ = 36.9) is also nicely reproduced by the calculations of the bridged, lithiated oxirane ($\Delta\delta$ = 54.8). Likewise, the lithiated benzofurans **1** and **2** ($\Delta\delta$ = 73.7 and 70.8, respectively) which have bridged structures in the solid state (see the structures of [**1** · O*i*Pr$_2$]$_2$, and [**2** · TMEDA]$_2$ in the introduction) agree well with the IGLO calculations of the bridged, lithiated furan ($\Delta\delta$ = 76.8). Most significantly, $LiCH_2OH$ with Li only attached to the carbon atom has been calculated to have a ^{13}C shift of $\Delta\delta = 6.3$, which is almost exactly the same ($\Delta\delta$ = 7.0) as found for **65** which contains a *chelate* dipole-stabilized five-membered ring instead of the C—O bond being bridged by lithium. Taken togehter, these experimental and IGLO-calculated results suggest that — except for special cases as e.g. chelate dipole-stabilized **65** (or **4**) — Li/oxygen carbenoids should have a *bridged* structure in solution, probably one which is similar to that of the calculated *bridged dimer* $[LiCH_2OH]_2$, see Scheme 18.

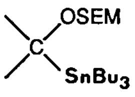
To sum up, the elongated C—O bonds in the lithiated ethers [**1** · O*i*Pr$_2$]$_2$, [**2** · TMEDA]$_2$, **3** · sparteine and **4** · 3 THF are in agreement with the calculations of $LiCH_2OH$ model structures, as outlined in detail earlier[1]. Corresponding to the elongated C—O bonds α-lithiated ethers react with nucleophiles like RLi, a reaction characteristic of Li/Hal carbenoids. These properties clearly demonstrate the Li/oxygen carbenoid nature of α-lithiated ethers. Furthermore, the downfield shift of the carbenoid ^{13}C atom in Li/Hal carbenoids is also observed in the Li/oxygen carbenoid series. A comparison of experimental ^{13}C values with calculated ones (IGLO) shows a nice agreement. The structure dependence of the experimental and calculated ^{13}C data lead to the conclusion that bridged dimers are the preferred species under normal conditions in solution.

We are very grateful to the *Deutsche Forschungsgemeinschaft* (Sonderforschungsbereich 260) and to the *Fonds der Chemischen Industrie* for supporting this work.

Experimental

All reactions were carried out in oven-dried glassware under dry argon. — Solvents: THF and ether were freshly distilled from potassium and sodium, respectively. — Products were purified by chromatography on Merck silica gel 60 (particle size 0.063—0.200 mm; eluents given in brackets) or by cyclochromatography on Merck silica gel 60 PF_{256} on a rotating chromatography disk (Chromatotron Modell 7924T, Harrison Research, USA; elution with a gradient from petroleum ether (boiling range: 40—60°C) to ether). Yields refer to analytically pure samples. — ^1H and ^{13}C NMR:

Bruker AC-300, AM-400, AMX-500; AB spectra: H_B refers to low- and H_A to high-field resonance. – Analytical gas chromatography: Siemens Sichromat 3 with a 30 m × 0.3 mm quartz capillary column with SE 52 (A). For quantitative analyses decane was used as internal standard. – Elemental analyses: Fachbereich Chemie der Universität Marburg. – Reagents: [D_8]THF and [D_{10}]diethyl ether were stored on molecular sieves (4 Å) under argon; *n*-butyllithium (*n*BuLi): 1.6 M in hexane; methyllithium (MeLi): 1.6 M in ether; *s*-butyllithium (*s*BuLi): 1.4 M in cyclohexane/isopentane (92:8); *tert*-butyllithium (*t*BuLi): 1.7 M in pentane; phenyllithium (PhLi): 2 M in cyclohexane/ether (70:30); [^{6}Li]*n*BuLi: 1.3 M in hexane[3d]. Solutions of [^{6}Li]*n*BuLi in [D_8]THF and [D_{10}]Et_2O were prepared by solvent exchange and used immediately. – Already published syntheses are only mentioned if changes had to be made or spectroscopic data were lacking.



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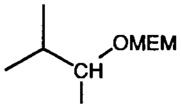
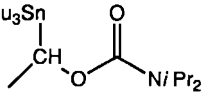


69



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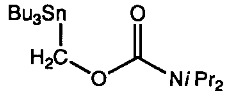

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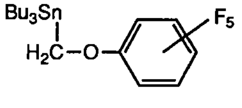

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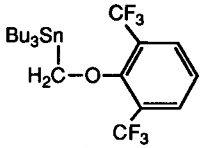
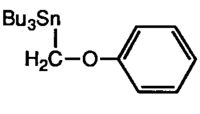


73



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2-(Tributylstannyl)-2-[2-(trimethylsilyl)ethoxymethoxy]propane (**68**): A solution of (tributylstannyl)lithium (11.8 mmol) was prepared according to the method of Still[43] from 1.65 ml (1.19 g, 11.8 mmol) of diisopropylamine, 7.36 ml (11.8 mmol) of *n*BuLi, and 3.17 ml (3.43 g, 11.8 mmol) of tributyltin hydride in 15 ml of THF. At −78 °C 0.85 ml (0.67 g, 11.8 mmol) of acetone was added dropwise via a syringe. After stirring for 5 min the mixture was poured into a satd. aqueous NH_4Cl solution (50 ml) and extracted with ether (3 × 50 ml). The combined organic layers were dried with $MgSO_4$, and the solvent was removed. The crude product was dissolved in CH_2Cl_2 (40 ml) and the solution treated with 8.20 ml (6.09 g, 47.1 mmol) of ethyldiisopropylamine and 5.00 ml (4.71 g, 28.3 mmol) of [2-(chloromethoxy)ethyl]trimethylsilane (SEMCl). After refluxing for 4 h the reaction mixture was poured into petroleum ether (100 ml) and washed successively with 0.5 N HCl (2 × 70 ml), water (100 ml), and a satd. aqueous $NaHCO_3$ solution (100 ml). Drying of the organic layer with Na_2SO_4, filtration, and removal of the solvent in vacuo gave a clear oil which was chromatographed on silica gel (petroleum ether/ether, 30:1) to afford pure **68** (2.95 g, 52%). – ^{1}H NMR ($CDCl_3$): δ = 0.05 (s, 11 H, 3 × $SiCH_3$, $SiCH_2$), 0.89 (m_c, 15 H, 3 × CH_2CH_3, 3 × $SnCH_2$), 1.30 (tq, both J = 7.4 Hz, 6 H, 3 × $CH_2CH_2CH_3$), 1.40 [s, 6 H, $C(CH_3)_2$], 1.51 (m_c, 6 H, 3 × $CH_2CH_2CH_2$), 3.60 (dd, J_1 = 8.1, J_2 = 8.9, 2 H, OCH_2CH_2), 4.68 (s, 2 H, OCH_2O). – ^{13}C NMR ($CDCl_3$): δ = −1.5 (3 × $SiCH_3$), 9.5 (3 × $SnCH_2$), 13.5 (3 × CH_2CH_3), 17.9 ($SiCH_2$), 27.5 (3 × $CH_2CH_2CH_3$), 28.9 [$C(CH_3)_2$], 29.3 (3 × $SnCH_2CH_2$), 65.1 (OCH_2-CH_2), 77.4 [$C(CH_3)_2$], 92.1 (OCH_2O). – $C_{21}H_{48}O_2SiSn$ (479.4): calcd. C 52.61, H 10.09; found C 52.41, H 10.12.

1-[(2-Methoxyethoxy)methoxy]-2-methyl-1-(tributylstannyl)-propane (**69**) was prepared as described for **68**. 3.45 ml (2.74 g, 38.0 mmol) of 2-methoxypropanal, (tributylstannyl)lithium [(38.0 mmol) prepared from 3.33 ml (3.85 g, 38.0 mmol) of diisopropylamine, 23.8 ml (38.0 mmol) of *n*BuLi, and 10.2 ml (11.1 g, 38.0 mmol) of tributyltin hydride in 80 ml of THF], 10.4 ml (7.70 g, 59.6 mmol) of ethyldiisopropylamine, and 6.80 ml (7.42 g, 59.6 mmol) of MEMCl were used; column chromatography on silica gel (petroleum ether/ether, 20:1) yielded **69** (6.20 g, 36%). – ^{1}H NMR ($CDCl_3$): δ = 0.88 [m_c, 21 H, 3 × CH_2CH_3, 3 × $SnCH_2$, $CH(CH_3)_2$], 1.25 (tq, both J = 7.5 Hz, 6 H, 3 × $CH_2CH_2CH_3$), 1.41 (m_c, 6 H, 3 × $CH_2CH_2CH_2$), 2.09 [m_c, 1 H, $CH(CH_3)_2$], 3.22 (s, 3 H, OCH_3), 3.48 (t, J = 4.7 Hz, 2 H, CH_2OCH_3), 3.54–3.70 (m, 2 H, $CH_2OCH_2CH_2$), 3.89 (d, J = 5.2, 1 H, OCH), AB signal ($δ_A$ = 4.54, $δ_B$ = 4.60, J_{AB} = 6.7, 2 H, OCH_2O). – ^{13}C NMR ($CDCl_3$): δ = 10.0 (3 × $SnCH_2$), 13.7 (3 × CH_2CH_3), 20.1, 21.1 [$CH(CH_3)_2$], 27.6 (3 × $CH_2CH_2CH_3$), 29.3 (3 × $SnCH_2CH_2$), 32.8 [$CH(CH_3)_2$], 59.1 (OCH_3), 67.2 (CH_2OCH_3), 71.9 ($CH_2OCH_2CH_2$), 82.4 (OCH), 96.0 (OCH_2O). – $C_{20}H_{44}O_3Sn$ (451.3): calcd. C 52.23, H 9.93; found C 52.56, H 9.89.

General Procedure for the Preparation of (Diisopropylcarbamoyloxy)(tributylstannyl)alkanes **70**, **71**: *1-(Diisopropylcarbamoyloxy)-1-(tributylstannyl)ethane* (**70**): To a solution of 18.8 ml (14.6 g, 125 mmol) of TMEDA and 85.7 ml (120 mmol) of *s*BuLi in ether (350 ml), cooled to −78 °C, was added dropwise 15.0 g (86.3 mmol) of (diisopropylcarbamoyloxy)ethane[44] in ether (70 ml). After stirring for 5 h 40.9 ml (49.1 g, 152 mmol) of tributyltin chloride was added, and the mixture was allowed to warm up to room temp. overnight. Quenching with 2 N HCl/ether (200 ml), extraction with ether (2 × 200 ml), drying with $NaHCO_3/Na_2SO_4$ (1:2), filtration, and evaporation of the solvent in vacuo yielded a residue which was purified by column chromatography on silica gel (petroleum ether/ether, 25:1) to furnish **70** (14.0 g, 35%). – ^{1}H NMR ($CDCl_3$): δ = 0.83 (m_c, 15 H, 3 × CH_2CH_3, 3 × $SnCH_2$), 1.14 [d, J = 7.5, 12 H, 2 × $CH(CH_3)_2$], 1.25 (tq, both J = 7.3 Hz, 6 H, 3 × $CH_2CH_2CH_3$), 1.44 (m_c, 9 H, 3 × $CH_2CH_2CH_2$, $CHCH_3$), 3.50, 4.16 [2 × m_c, 2 × 1 H, 2 × $CH(CH_3)_2$], 4.68 (q, J = 7.6, 1 H, $CHCH_3$). – ^{13}C NMR ($CDCl_3$): δ = 9.4 (3 × $SnCH_2$), 13.6 (3 × CH_2CH_3), 20.2 ($CHCH_3$), 21.0 [2 × $CH(CH_3)_2$], 27.5 (3 × $CH_2CH_2CH_3$), 29.1 (3 × $SnCH_2CH_2$), 45.6 [2 × $CH(CH_3)_2$], 68.4 ($CHCH_3$), 156.1 (C=O). – $C_{21}H_{45}NO_2Sn$ (462.3): calcd. C 54.56, H 9.81, N 3.03; found C 54.53, H 9.76, N 2.90.

(Diisopropylcarbamoyloxy)(tributylstannyl)methane (**71**) was prepared as described for **70**. 5.00 g (31.4 mmol) of (diisopropylcarbamoyloxy)methane[45], 25.0 ml (35.0 mmol) of *s*BuLi, 5.20 ml (4.03 g, 34.7 mmol) of TMEDA in ether (100 ml), and 10.0 ml (12.0 g, 36.9 mmol) of tributyltin chloride gave after column chromatography on silica gel (petroleum ether/ether, 10:1) **71** (5.98 g, 43%). – ^{1}H NMR ($CDCl_3$): δ = 0.83 (m_c, 15 H, 3 × CH_2CH_3, 3 × $SnCH_2$), 1.12 [d, J = 6.8 Hz, 12 H, 2 × $CH(CH_3)_2$], 1.24 (tq, both J = 7.3 Hz, 6 H, 3 × $CH_2CH_2CH_3$), 1.44 (m_c, 6 H, 3 × $CH_2CH_2CH_2$), 3.81 [m_c, 2 H, 2 × $CH(CH_3)_2$], 4.05 (s, $J_{Sn,H}$ = 11.3 Hz, 2 H, OCH_2). – ^{13}C NMR ($CDCl_3$): δ = 9.5 (3 × $SnCH_2$), 13.6 (3 × CH_2CH_3), 20.9 [2 × $CH(CH_3)_2$], 27.3 (3 × $CH_2CH_2CH_3$), 29.0 (3 × $SnCH_2CH_2$), 45.6 [2 × $CH(CH_3)_2$], 55.0 (OCH_2), 156.8 (C=O). – $C_{20}H_{43}NO_2Sn$ (*448.3*): calcd. C 53.59, H 9.67, N 3.13; found C 53.58, H 9.82, N 3.55.

General Procedure for the Preparation of (Aryloxymethyl)tributylstannanes **72**–**74**: *Tributyl[(pentafluorophenoxy)methyl]stannane* (**72**): 6.68 g (15.5 mmol) of tributyl(iodomethyl)stannane[46], 5.00 g (27.2 mmol) of 2,3,4,5,6-pentafluorophenol, and 2.14 g (15.5 mmol) of K_2CO_3 were dissolved in acetone (100 ml), and the solution was refluxed for 7 d. The reaction mixture was poured into water (100 ml) and extracted with ether (3 × 50 ml). The combined organic layers were washed with 2 N NaOH (2 × 50 ml), dried with Na_2SO_4, filtrated, and the solvent was removed in vacuo. Purification of the crude product by column chromatography on silica gel (petroleum ether/ether, 20:1) furnished **72** (5.71 g, 76%). – ^1H NMR ($CDCl_3$): $\delta = 0.93$ (t, $J = 7.3$ Hz, 9H, 3 × CH_2CH_3), 1.00 (m_c, 6H, 3 × $SnCH_2$), 1.35 (tq, both $J = 7.4$ Hz, 6H, 3 × $CH_2CH_2CH_3$), 1.56 (m_c, 6H, 3 × $CH_2CH_2CH_2$), 4.48 (s, $J_{Sn,H} = 14.6$ Hz, 2H, CH_2O). – ^{13}C NMR ($CDCl_3$): $\delta = 8.9$ (3 × $SnCH_2$), 13.4 (3 × CH_2CH_3), 27.1 (3 × $CH_2CH_2CH_3$), 29.0 (3 × $SnCH_2CH_2$), 69.0 (OCH_2), 136.9 (d, $J_{C,F} = 247.4$ Hz, aromat. C), 137.8 (d, $J_{C,F} = 250.3$ Hz, aromat. C), 138.5 (d, $J_{C,F} = 238.3$ Hz, aromat. C), 143.3 (aromat. C). – $C_{19}H_{29}F_5OSn$ (487.1): calcd. C 46.85, H 6.00; found C 47.04, H 6.18.

{[3,5-Bis(trifluoromethyl)phenoxy]methyl}tributylstannane (**73**): 5.00 g (21.7 mmol) of 3,5-Bis(trifluoromethyl)phenol, 5.39 g (12.5 mmol) of tributyl(iodomethyl)stannane[46], and 1.73 g (12.5 mmol) of K_2CO_3 in acetone (100 ml) were allowed to react to furnish **73** (5.42 g, 81%; b.p. 96–100°C/0.01 Torr). – ^1H NMR ($CDCl_3$): $\delta = 0.90$ (t, $J = 7.3$ Hz, 9H, 3 × CH_2CH_3), 1.01 (dd, $J_1 = 7.9$, $J_2 = 8.1$ Hz, 6H, 3 × $SnCH_2$), 1.29 (tq, both $J = 7.4$ Hz, 6H, 3 × $CH_2CH_2CH_3$), 1.36 (m_c, 6H, 3 × $CH_2CH_2CH_2$), 4.15 (s, $J_{Sn,H} = 15.3$ Hz, 2H, OCH_2), 7.20–7.35 (m, 3H, aryl-H). – ^{13}C NMR ($CDCl_3$): $\delta = 9.2$ (3 × $SnCH_2$), 13.5 (3 × CH_2CH_3), 27.2 (3 × $CH_2CH_2CH_3$), 28.9 (3 × $SnCH_2CH_2$), 59.5 (OCH_2), 113.5, 113.6, 114.3, 121.5, 125.1, 132.3, 132.7 (aromat. CH, aromat. C, 2 × CF_3), 162.3 (aromat. C). – $C_{21}H_{32}F_6OSn$ (533.2): calcd. C 47.23, H 6.00; found C 47.15, H 6.30.

Tributyl(phenoxymethyl)stannane[47](**74**): 46.7 g (109 mmol) of tributyl(iodomethyl)stannane[46], 20.4 g (217 mmol) of phenol, and 15.0 g (109 mmol) of K_2CO_3 in acetone (400 ml) were allowed to react to furnish after distillation (b.p. 110°C/0.01 Torr) **74** (36.1 g, 84%). – ^1H NMR ($CDCl_3$): $\delta = 0.96$ (m_c, 15H, 3 × CH_2CH_3, 3 × $SnCH_2$), 1.36 (tq, both $J = 7.4$ Hz, 6H, 3 × $CH_2CH_2CH_3$), 1.57 (m_c, 6H, 3 × $CH_2CH_2CH_2$), 4.21 (s, $J_{Sn,H} = 14.3$ Hz, 2H, CH_2O), 6.94–7.01 (m, 3H, aryl-H), 7.27–7.34 (m, 2H, aryl-H). – $C_{19}H_{34}OSn$ (397.2): calcd. C 57.46, H 8.63; found C 57.14, H 8.64. – On the basis of the ^1H-NMR spectral and the elemental analysis the compound corresponded in all respects to the compound described in ref.[47]

Tributyl(1,3-dioxan-2-yl)stannane[21], *(methoxymethoxy)(tributylstannyl)methane*[32], *tributyl(chloromethyl)stannane*[46], *tributyl(tetrahydropyran-2-yl)stannane*[48], *1-methoxy-2-methyl-1-(tributylstannyl)propane*[49], and *(epoxyethyl)triphenylsilane*[50].

Reactions with Nucleophiles

General Procedure for the Reactions of the (Aryloxy)methyllithium Compounds **22** *and* **25** *with PhLi*: 1–2 mmol of tributylstannyl ether was dissolved in 3 ml of ether or THF, the solution cooled to –78°C and treated with 1.1 mol. equiv. of *n*BuLi. After 30 min 2–3 mol. equiv. of PhLi was added dropwise, and the mixture was kept at the given temp. for the specified time, see Tables 3 and 4. Addition of water (20 ml), extraction with ether (3 × 10 ml), washing of the organic layers with 2 N NaOH (3 × 50 ml) and water (3 × 20 ml), drying with Na_2SO_4 and filtration furnished a solution which was directly analyzed by GC.

Phenol (**24**) was quantitatively determined in a separate experiment: The lithiated ether **22** was treated with PhLi as described above. After addition of water followed by ether extraction the organic layer was washed with 2 N HCl (3 × 50 ml) and dried with Na_2SO_4. Removal of the solvent in vacuo gave the crude phenol, which was purified by cyclochromatography. Concerning reaction conditions, yields of toluene (**23**) and phenol (**24**), see Tables 3 and 4, respectively[47].

Table 3. Reactions of the lithiated ether **22** with PhLi (**5**)

Mol-equiv. of 5	Solvent	Temp. [°C]	Time [h]	Yield [%] of **23**	**24**
2	Et2O	-78	2.3	0.4-6	9
2	Et2O	-28	3	21	48
3	Et2O	0	3	29	51
3	Et2O	25	3	39	94
3	THF	-78	3	5	14
3	THF	-28	3	29	
3	THF	0	3	15	
3	THF	25	3	13	

Table 4. Reactions of the lithiated ether **25** with PhLi (**5**)

Mol-equiv. of **5**	Solvent	Temp. [°C]	Time [h]	Yield [%] of **23**
3	Et2O	-78	3	53
3	Et2O	-28	3	19
3	Et2O	0	3	13
3	Et2O	25	3	13
3	THF	-78	3	-
3	THF	-28	3	-
3	THF	0	3	-

General Procedure for the Reactions of (Carbamoyloxy)methyllithium **49** *with PhLi* (**5**): A solution of 0.45 g (1.00 mmol) of **71** in Et_2O (3.00 ml) was cooled to –120°C and treated dropwise with 0.69 ml (1.10 mmol) of *n*BuLi. After 30 min 1.50 ml (3.00 mmol) of PhLi was added dropwise, and the mixture was kept at the given temp. (see Table 5) for 3–3.5 h. Workup as described above was followed by quantitative GC analysis.

Table 5. Reactions of the lithiated carbamoyloxy compound **49** with PhLi (**5**)

Mol-equiv. **5**	Solvent	Temp. [°C]	Time [h]	Yield [%] of **23**
3	Et2O	-120	3	10
3	Et2O	-78	3.5	10
3	Et2O	-78/-28	0.5/3	3

General Procedure for the Reactions of 2-Lithio-1,3-dioxane (**34**) *with PhLi* (**5**): To a solution of 0.55 g (1.49 mmol) of tributyl-(1,3-dioxane-2-yl)stannane in THF or ether (3.00 ml) cooled to –78°C was slowly added 1.03 ml (1.64 mmol) of *n*BuLi. After 1 h 2.24 ml (4.47 mmol) of PhLi was added, and the mixture was immediately warmed to the temp. given in Table 6. The reaction was quenched after 3 h with phosphate buffer pH 7 (50 ml), the mixture was extracted with ether (3 × 50 ml), the combined extracts were dried with Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by cyclochromatography yielding 3-(benzyloxy)-1-propanol (**38**). – ^1H NMR ($CDCl_3$): $\delta = 1.84$ (quint, $J = 5.7$ Hz, 2H, $CH_2CH_2CH_2$), 2.32 (m_c, 1H, OH), 3.63 (t, $J = 5.8$ Hz, 2H, OCH_2CH_2), 3.76 (q, $J = 5.5$ Hz, 2H, $HOCH_2CH_2$), 4.49 (s, 2H, $C_6H_5CH_2O$), 7.30 (m_c, 5H, aryl-H). – $C_{10}H_{14}O_2$: calcd. 166.0994, found 166.0994 (MS). — On the basis of ^{1}H-NMR spectroscopic and high-resolution mass spectral data the compound corresponded in all respects to the compound described in ref.[51]

Table 6. Reactions of the lithiated dioxane **34** with PhLi (**5**)

Mol-equiv. of **5**	Solvent	Temp. [°C]	Time [h]	Yield [%] of **38**
3	Et$_2$O	-78	3	10
3	Et$_2$O	-28	3.5	25
3	Et$_2$O	0	3.5	8
3	Et$_2$O	25	3	6
3	THF	-28	3	2
3	THF	0	3	2

General Procedure for the Reactions of 2-Lithiobenzofuran **2** *with PhLi* (**5**): 1.88 ml (3.00 mmol) of *n*BuLi was added dropwise to a solution of 354 mg (3.00 mmol) of benzofuran and 0.45 ml (349 mg, 3.00 mmol) of TMEDA in ether (3.00 ml). After stirring for 30 min the reaction mixture was cooled to 0°C, then 3.00 ml (6.00 mmol) of PhLi was added dropwise. The solution was stirred for 3 h at room temp. and the reaction quenched with 0.27 ml (15.0 mmol) of H_2O. The mixture was poured into an aqueous NH_4Cl solution (50 ml), extracted with ether (3 × 30 ml), the combined extracts were dried with $MgSO_4$, concentrated, and the residue was purified by cyclochromatography. For yields, see Scheme 12 and ref.[25]

General Procedure for Reactions of Diphenyl(trimethylsilyloxy)-methyllithium **4** *with Alkyllithium Compounds in THF:* A solution of 513 mg (2.00 mmol) of diphenyl(trimethylsilyloxy)methane[52] in THF (3.00 ml) was cooled to −78°C, then 1.57 ml (2.20 mmol) of *s*BuLi was added dropwise. This solution was maintained at −28°C for 6 h, chilled to −78°C, and 10.0 mmol of alkyllithium compound was added dropwise. After 30 min the reaction mixture was warmed up to the given temp. for the specified time (see Table 7). The reaction was then quenched with 0.54 ml (0.60 g, 30.0 mmol) of D_2O, the mixture warmed up to room temp. overnight, poured into a satd. aqueous NaCl solution (50 ml) and extracted with Et_2O (3 × 20 ml). The combined organic layers were washed with water (3 × 50 ml) and dried with $MgSO_4$. Purification of the crude products obtained by evaporation of the solvents from the extracts was effected by cyclochromatography.

Table 7. Reactions of the lithiated ether **4** · 3 THF with alkyllithium compounds in THF

Mol-equiv. of AlkylLi	Temp. [°C]	Time [h]	Yield [%] of [1-D]**75**[a]	 **76**[b]	 [1-D]**52**[c]
5 MeLi	-28	6	49	30	-
5 *n*BuLi	-28	6	31	24	-
5 *s*BuLi	-28	6	44	8	-
5 *t*BuLi	-28	6	24	18	-
5 MeLi	25	3	28	12	-
5 *n*BuLi	-25	3	23	39	-
5 *s*BuLi	-25	3	26	-	-
5 *t*BuLi	-25	3	23	-	-
5 MeLi	25	96	6	21	-
5 MeLi	67	1	23	-	-

[a] [1-D]**75**: [1-D]diphenyl(trimethylsilyloxy)methane. — [b] **76**: [1-D]Diphenylmethanol (with 35−75% D incorporation). — [c] [1-D]**52**: [1-D]diphenyl(alkyl)methane.

General Procedure for Reactions of Diphenyl(trimethylsilyloxy)-methyllithium **4** · 3 THF *with Alkyllithium Compounds in Solvents other than THF:* A solution of 513 mg (2.00 mmol) diphenyl(trimethylsilyloxy)methyllithium **4** in THF (3.00 ml) was prepared as described above. After removal of the solvent in vacuo 10.0 mmol of alkyllithium compound was added dropwise at −78°C. After 1 h the mixture was warmed up to −28°C overnight and left at room temp. for at least 4 d. Workup as described above was followed by cyclochromatography. For obtained yields, see Table 8.

Table 8. Reactions of the lithiated ether **4** · 3 THF with alkyllithium compounds in solvents other than THF

Mol-equiv. of AlkylLi	Solvent	Temp. [°C]	Time [h]	Yield [%] of [1-D]**75**[a]	 **76**[b]	 [1-D]**52**[c]
5 MeLi	Et$_2$O	-28/25	16/96	6	21	-
5 *n*BuLi	hexane	-28/25	16/96	36	20	-
5 *s*BuLi	cyclohexane /isopentane	-28/25	16/96	10	24	-
5 *t*BuLi	pentane	-28/25	16/96	40	8	-

[a] [1-D]**75**: [1-D]diphenyl(trimethylsilyloxy)methane. — [b] **76**: [1-D]diphenylmethanol (with ≤70% D incorporation). — [c] [1-D]**52**: [1-D]diphenyl(alkyl)methane.

NMR Spectroscopy

Preparation of the NMR samples: A solution of 0.50−0.80 mmol of the corresponding ether in 0.30 ml [D$_8$]THF or [D$_{10}$]Et$_2$O was placed in a NMR tube, and argon was bubbled through the solution using a 30-cm steal needle. After cooling the solution to −80 to −120°C 1.10 mol. equiv. of [^{6}Li]*n*BuLi in [D$_8$]THF or [D$_{10}$]Et$_2$O were added dropwise via a syringe. The solution was mixed by means of a slow argon stream.

☆ Dedicated to Professor *Reinhard W. Hoffmann* on the occasion of his 60th birthday.

[1] [1a] G. Boche, A. Opel, M. Marsch, K. Harms, F. Haller, J. C. W. Lohrenz, C. Thümmler, W. Koch, *Chem. Ber.* **1992**, *125*, 2265−2273. — [1b] G. Boche, J. C. W. Lohrenz, A. Opel in *Lithium Compounds: Principles and Applications* (Eds.: P. von R. Schleyer, A.-M. Sapse), J. Wiley & Sons, New York, in print.

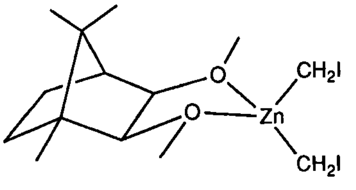
[2] S. Harder, J. Boersma, L. Brandsma, J. A. Kanters, W. Bauer, R. Pi, P. von R. Schleyer, H. Schöllhorn, U. Thewalt, *Organomet.* **1989**, *8*, 1688−1696; see also S. Harder, Dissertation, University of Utrecht, **1990**.

[3] [3a] H. Siegel, K. Hiltbrunner, D. Seebach, *Angew. Chem.* **1979**, *91*, 844−845; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 784. — [3b] D. Seebach, H. Siegel, K. Müllen, K. Hiltbrunner, *Angew. Chem.* **1979**, *91*, 845−846; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 785. — [3c] D. Seebach, H. Siegel, J. Gabriel, R. Hässig, *Helv. Chim. Acta* **1980**, *63*, 2046−2053. — [3d] D. Seebach, R. Hässig, J. Gabriel, *Helv. Chim. Acta* **1983**, *66*, 308−337.

[4] [4a] T. Clark, P. von R. Schleyer, *J. Chem. Soc., Chem. Commun.* **1979**, 883−884. — [4b] T. Clark, P. von R. Schleyer, *Tetrahedron Lett.* **1979**, 4963−4966. — [4c] T. Clark, P. von R. Schleyer, *J. Am. Chem. Soc.* **1979**, *101*, 7747−7748. — [4d] C. Rohde, T. Clark, E. Kaufmann, P. von R. Schleyer, *J. Chem. Soc., Chem. Commun.* **1982**, 882−884. — [4e] M. A. Vincent, H. F. Schaefer III, *J. Chem. Phys.* **1982**, *77*, 6103−6108. — [4f] B. T. Luke, J. A. Pople, P. von R. Schleyer, T. Clark, *Chem. Phys. Lett.* **1983**, *102*, 148−154. — [4g] J. Mareda, N. G. Rondan, K. N. Houk, T. Clark, P. von R. Schleyer, *J. Am. Chem. Soc.* **1983**, *105*, 6997−6999. — [4h] P. von 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, and cited literature. — [4i] B. Wang, C. Deng, *Chem. Phys. Lett.* **1988**, *147*, 99−104. — [4j] B. Wang, C. Deng, L. Xu, T. Tao, *Chem. Phys. Lett.* **1989**, *161*, 388−392.

[5] T. Clark, P. von R. Schleyer, K. N. Houk, N. G. Rondan, *J. Chem. Soc., Chem. Commun.* **1981**, 579–581.

[6] The experimental proof in the Li/*halide* series has been lacking: The following "Wittig-Furukawa" reagent, which so far comes closest to a Li/Hal carbenoid, has C–I bond lengths between 213 and 221 pm which is in the range of normal C–I bonds (214–221 pm), see S. E. Denmark, J. P. Edwards, S. R. Wilson, *J. Am. Chem. Soc.* **1991**, *113*, 723–725.



[7] Reviews on carbenoids: [7a] W. Kirmse, *Angew. Chem.* **1965**, *77*, 1–64; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1. – [7b] G. Köbrich, *Angew. Chem.* **1967**, *79*, 15–27; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 41. – [7c] G. Köbrich, *Angew. Chem.* **1972**, *84*, 557–570; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 473. – [7d] H. Siegel, *Top. Curr. Chem.* **1982**, *106*, 55–78.

[8] [8a] A. Lüttringhaus, G. v. Sääf, *Angew. Chem.* **1938**, *51*, 915–920; see also [8b] A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker, G. Borth, *Liebigs Ann. Chem.* **1947**, *557*, 46–69.

[9] G. Wittig, L. Löhmann, *Liebigs Ann. Chem.* **1942**, *550*, 260–268.

[10] U. Schöllkopf, M. Eisert, *Liebigs Ann. Chem.* **1963**, *664*, 76–88.

[11] K. Ziegler, H.-G. Gellert, *Liebigs Ann. Chem.* **1950**, *567*, 185–195.

[12] H. Hoberg, *Liebigs Ann. Chem.* **1962**, *656*, 1–14.

[13] [13a] Review: A. Maercker, *Angew. Chem.* **1987**, *99*, 1002–1019; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 972. – [13b] A. Maercker, *Liebigs Ann. Chem.* **1969**, *730*, 91–99. – [13c] A. Maercker, W. Demuth, *Angew. Chem.* **1973**, *85*, 90–92; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 75. – [13d] A. Maercker, W. Demuth, *Liebigs Ann. Chem.* **1977**, 1909–1937.

[14] A. C. Cope, G. A. Berchtold, P. E. Peterson, S. H. Sharman, *J. Am. Chem. Soc.* **1960**, *82*, 6370–6372; see also A. C. Cope, M. Brown, H.-H. Lee, *ibid.* **1958**, *80*, 2855–2859; A. C. Cope, H.-H. Lee, H. E. Petree, *ibid.* **1958**, *80*, 2849–2852.

[15] [15a] J. K. Crandall, L.-H. C. Lin, *J. Am. Chem. Soc.* **1967**, *89*, 4526–4527. – [15b] Detailed review: J. K. Crandall, M. Apparu, *Org. React.* **1983**, *29*, 345–443.

[16] [16a] J. J. Eisch, J. E. Galle, *J. Am. Chem. Soc.* **1976**, *98*, 4646–4648. – [16b] J. J. Eisch, J. E. Galle, *J. Organomet. Chem.* **1988**, *341*, 293–313. – [16c] J. J. Eisch, J. E. Galle, *J. Org. Chem.* **1990**, *55*, 4835–4840.

[17] G. A. Molander, K. Mautner, *J. Org. Chem.* **1989**, *54*, 4042–4050.

[18] P. Lohse, H. Loner, P. Acklin, F. Sternfeld, A. Pfaltz, *Tetrahedron Lett.* **1991**, *32*, 615–618.

[19] M. Taniguchi, K. Oshima, K. Utimoto, *Tetrahedron Lett.* **1991**, *32*, 2783–2786.

[20] J. A. Soderquist, C. Lopez, *Tetrahedron Lett.* **1991**, *32*, 6305–6306.

[21] C. S. Shiner, T. Tsunoda, B. A. Goodman, S. Ingham, S. Lee, P. E. Vorndam, *J. Am. Chem. Soc.* **1989**, *111*, 1381–1392.

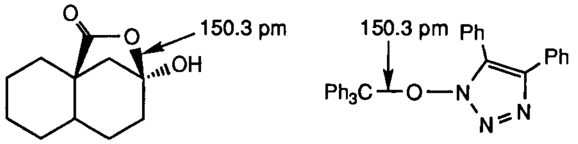
[22] [22a] F. L. M. Pattison, R. E. A. Dear, *Can. J. Chem.* **1963**, *41*, 2600–2606. – [22b] M. Stähle, J. Hartmann, M. Schlosser, *Helv. Chim. Acta* **1977**, *60*, 1730–1738. The first example seems to have been a MgBr/oxygen carbenoid, see C. M. Hill, G. W. Senter, L. Haynes, M. E. Hill, *J. Am. Chem. Soc.* **1954**, *76*, 4538–4539.

[23] [23a] Review: P. Kocieński, C. Barber, *Pure & Appl. Chem.* **1990**, *62*, 1933–1940. – [23b] P. Kocieński, S. Wadman, K. Coopper, *J. Am. Chem. Soc.* **1989**, *111*, 2363–2365.

[24] M. Duraisamy, H. M. Walborsky, *J. Am. Chem. Soc.* **1984**, *106*, 5035–5037. See also: M. Topolski, M. Duraisamy, J. Rachoń, J. Gawronski, K. Gawronska, V. Goedken, H. M. Walborsky, *J. Org. Chem.* **1993**, *58*, 546.

[25] T. Nguyen, E. Negishi, *Tetrahedron Lett.* **1991**, *32*, 5903–5906. We would also like to mention that in the CuCN-catalyzed reactions we have similarly not been able to obtain substitution products **47** with *s*BuLi and *t*BuLi, while CH$_3$Li, *n*BuLi and PhLi gave higher yields of **47** than in the non-catalyzed reactions. A possible reason for the different results could be TMEDA which was present in our experiments. TMEDA could favor deprotonation reactions of *s*BuLi and *t*BuLi. We are grateful to a referee for this hint.

[26] Other compounds with long C–O bonds are also prone to facile substitution reactions with nucleophiles as e.g.:



D. J. Chadwick, J. D. Dunitz, *J. Chem. Soc., Perkin Trans. 2,* **1979**, 276–284; C. J. Arceneaux, J. H. Boyer, C. L. Klein, E. D. Stevens, *Acta Crystallogr., Sect. C,* **1990**, *46*, 146–148. [For a thorough discussion of the relation between bond weakening and bond length (of C–C bonds), see Ch. Rüchardt, H. D. Beckhaus, *Top. Curr. Chem.* **1986**, *130*, 1–22.]

[27] S. Harder has calculated mixed dimers of furanyllithium with LiH[2]; a LiCH$_2$F · LiF-mixed dimer was calculated by Schleyer et al.[4d]; model calculation of the reaction of a carbenoid with an olefin, see ref.[4g]; the Fritsch-Buttenberg-Wiechell rearrangement was calculated by Wang and Deng[4i].

[28] [28a] M. Marsch, K. Harms, O. Zschage, D. Hoppe, G. Boche, *Angew. Chem.* **1991**, *103*, 338–339; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 321–323, and references cited. – [28b] Short review of D. Hoppe's work, see P. Knochel, *Angew. Chem.* **1992**, *104*, 1486–1488; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1459–1461.

[29] T. E. Hogen-Esch, J. Smid, *J. Am. Chem. Soc.* **1966**, *88*, 307–318; 318–324.

[30] G. Wittig, E. Stahnecker, *Liebigs Ann. Chem.* **1957**, *605*, 69–93.

[31] M. Schlosser, *Struktur und Reaktivität polarer Organometalle*, Springer Verlag, Berlin, **1973**, p. 28/29. I am very grateful to Professor Schlosser for bringing these results to my mind (1–26–1993).

[32] C. Nayera, M. Yus, R. Hässig, D. Seebach, *Helv. Chim. Acta* **1984**, *67*, 1100–1103.

[33] G. Boche, F. Bosold, P. Zulauf, M. Marsch, K. Harms, J. Lohrenz, *Angew. Chem.* **1991**, *103*, 1497–1499; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1455–1457.

[34] The α-triphenylsilyl-substituted **64** displays not only a downfield shift of the signal of the α-carbon atom but also of C_β ($\Delta\delta$ = 10.4), which could be due to the slight elongation also of the C–C bond as calculated for **67**, see Scheme 17. Interestingly, this C_β shift is reproduced by IGLO(II+sp)//MP2/6-311++G(d,p) calculations of lithiated oxirane ($\Delta\delta$ = 17.6) as well as α-lithiated ethanol [IGLO(II+sp)//HF/6-311++G-(d,p); $\Delta\delta = 8.9$]. All attempts to measure the NMR spectrum of a lithiated oxirane without an anion-stabilizing substituent at the lithiated C atom so far failed.

[35] W. Bauer, W. R. Winchester, P. von R. Schleyer, *Organomet.* **1987**, *6*, 2371–2379.

[36] W. Bauer, F. Hampel, *J. Chem. Soc., Chem. Commun.* **1992**, 903–905.

[37] The formation of monomers in the solid state structures of **3** · sparteine and **4** · 3 THF could be due to steric reasons. In the crystal structure of (1*S*)-1-(*N*-pivaloyl-*N*-methyl)benzyllithium · (–)-sparteine likewise a monomer is found; G. Boche, M. Marsch, J. Halbach, K. Harms, B. Ledig, F. Schubert, J. C. W. Lohrenz, H. Ahlbrecht, *Chem. Ber.* **1993**, *126*, 1887, following.

[38] Preliminary cryoscopic measurements of the aggregation of **59** in THF at –108 °C lead to $n = 2.2-2.9$, which would indicate the presence of higher aggregates besides the dimer; the only formation of monomers is excluded: F. Haller, Dissertation in progress, Universität Marburg.

[39] Earlier Schleyer et al. found a dimer of LiCH$_2$F which had dimerized along the C–F bonds[4d].

[40] [40a] W. Kutzelnigg, *Isr. J. Chem.* **1980**, *19*, 193–200. – [40b] M. Schindler, W. Kutzelnigg, *J. Chem. Phys.* **1982**, *76*, 1919–1923. – [40c] W. Kutzelnigg, *J. Mol. Struct. (THEOCHEM)* **1989**, *202*, 11–61. – [40d] Review: W. Kutzelnigg, U. Fleischer, M. Schindler, *NMR, Basic Principles and Progress*, Springer, New York, **1990**, vol. 23, p. 165–262.

[41] [41a] M. Schindler, *J. Am. Chem. Soc.* **1987**, *109*, 1020–1033. – [4b] See also K. B. Wiberg, C. M. Hadad, S. Sieber, P. von R. Schleyer, *J. Am. Chem. Soc.* **1992**, *114*, 5820–5828, and cited literature.

[42] [42a] M. Bühl, N. J. R. van Eikema Hommes, P. von R. Schleyer, U. Fleischer, W. Kutzelnigg, *J. Am. Chem. Soc.* **1991**, *113*,

2459 – 2465. – [42b] L. A. Paquette, W. Bauer, M. R. Sirik, M. Bühl, M. Feigel, P. von R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 8776 – 8789.

[43] W. C. Still, *J. Am. Chem. Soc.* **1978**, *100*, 1481 – 1487.

[44] O. Hoshino, K. Saito, M. Ishizaki, B. Umezawa, *Synth. Commun.* **1987**, *17*(16), 1887 – 1892.

[45] A. P. N. Franchimont, H. Friedmann, *Recl. Trav. Chim. Pays-Bas* **1905**, *24*, 404 – 418.

[46] D. E. Seitz, J. J. Carroll, C. P. Cartaya, S.-H. Lee, A. Zapata, *Synth. Commun.* **1983**, *13*, 129 – 134.

[47] J. J. Eisch, J. E. Galle, A. Piotrowski, M.-R. Tsai, *J. Org. Chem.* **1982**, *47*, 5051 – 5056. – We would like to mention that Eisch had prepared $PhOCH_2Li$ (**22**) earlier and observed α-elimination to give phenol; furthermore small amounts of toluene, ethylbenzene, and *n*-butylbenzene were formed in the presence of phenyllithium; these were considered as PhLi-trapping products of methylene and ethylene generated in the α-elimination of $PhOCH_2Li$ (**22**).

[48] J. S. Sawyer, A. Kucerovy, T. L. Macdonald, G. J. McGarvey, *J. Am. Chem. Soc.* **1988**, *110*, 842 – 853.

[49] R. Hirsch, Dissertation in progress, Universität Marburg.

[50] J. J. Eisch, J. J. Trainor, *J. Org. Chem.* **1963**, *28*, 487 – 492.

[51] [51a] G. M. Bennett, A. L. Hock, *J. Chem. Soc., Trans.* **1927**, 472 – 476. – [51b] H. Thies, R. Wolfschütz, G. Frenking, J. Schmidt, H. Schwarz, *Tetrahedron* **1982**, *38*, 1647 – 1656.

[52] A. Wright, R. West, *J. Am. Chem. Soc.* **1974**, *96*, 3214 – 3222.

[67/93]