Organometallics 1990, *9*, 511–516 511

Geometries. Table VI compares the calculated (AM1) geometries with experiment. The mean unsigned error in bond lengths is 0.12 Å, and the signed error −0.10 Å. The calculated aluminum bond lengths are thus systematically too short, a tendency already noted in AM1.[4] AM1, like MNDO,[7] predicts the linear (Al–O–Al–O) forms of both Al_2O_2 and $Al_2O_2^+$ to be more stable than the previously assumed square-planar structures, while AlOH is predicted to be linear rather than bent. Further studies of these molecules would be of interest.

Conclusions. We have produced a useful set of AM1 parameters for aluminum. The results from calculations using our values are generally closer to experimental than either MNDO or Stewart's newly introduced PM3.

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Isolation and Crystal Structure of a Presumed Intermediate in the Reaction of an Organolithium Compound with an Epoxide

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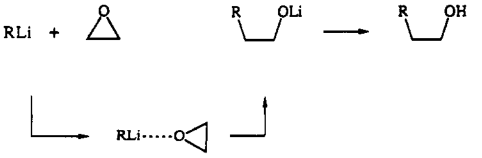
The organolithium–epoxide complexes tetrakis(1-lithio-2-methoxybenzene)–bis(ethylene oxide) and tetrakis(1-lithio-2-methoxybenzene)–bis(propylene oxide), which are thought to be intermediates in the β-hydroxyalkylation of organolithium compounds, have been isolated and characterized. NMR studies on these complexes in nonpolar solvents such as benzene and toluene provide evidence for epoxide oxygen to lithium coordination. Additionally, the propylene oxide complex has been characterized by single-crystal X-ray diffraction at 100 K. The compound crystallizes in the triclinic system (space group $P\bar{1}$) with chemical formula $4[C_7H_7OLi]\cdot 2[C_3H_6O]$ and $Z = 2$. Cell dimensions: $a = 11.348$ (1) Å, $b = 12.043$ (1) Å, $c = 12.099$ (1) Å, $\alpha = 95.57$ (1)°, $\beta = 92.30$ (1)°, $\gamma = 97.52$ (1)°. The structure consists of a tetrameric aggregate of 1-lithio-2-methoxybenzene and two disordered propylene oxide molecules, which coordinate to lithium as external Lewis bases. Since ab initio calculations (RHF; SV 3-21G) show the activation of the epoxide by lithium coordination to be very small, the question of whether such complexes are intermediates in the nucleophilic ring opening of epoxides remains unanswered.

Introduction

The introduction of a β-hydroxyalkyl group by reaction of a nucleophilic species with an epoxide is an important synthetic operation. Depending upon the nature of the nucleophile and the structure of the epoxide, this reaction is carried out in different solvent systems[1] (eq 1 and 2).



(1)

(2)

This nucleophilic ring opening of epoxides is assumed to be facilitated by electrophilic assistance by acids, protic solvents, or Lewis acids.[2,3] It was found that the acid-catalyzed ring opening of ethylene oxide (EO) proceeds via the protonated species.[3,4] Ab initio calculations[4] (STO-5G) have shown this oxonium cation to be activated toward nucleophilic ring opening since (i) its C–O bond is elongated (and presumably weakened) compared to that in EO and (ii) the calculated electron density on the carbon atoms of EO decreases upon protonation.

In analogy with the acid-catalyzed ring opening, it is generally assumed that the reaction of an epoxide with an organolithium compound in solvents such as diethyl ether and tetrahydrofuran (THF) is assisted by coordination of the epoxide toward lithium.[5] This assumption seems

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Table I. ^{1}H NMR Data for the Ethylene Ocide (EO) Signal in 1-Lithio-2-methoxybenzene (1b)–EO (2/1) and 1-Lithio-2-*tert*-butoxybenzene (3b)–EO (2/1) Dissolved in Toluene-d_8 at Different Temperatures

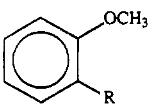
	T, K														
	193	203	213	223	233	243	253	263	273	283	293	303	313	323	333
δ (**1b**–EtO), ppm	1.37	1.39	1.41	1.44	1.47	1.50	1.53	1.56	1.60	1.64	1.66	1.70	1.74	1.77	1.80
bonded EO, %[a]	91	89	87	84	80	77	74	71	66	62	60	55	51	48	45

	T, K[b]						
	303	313	323	333	343	353	363
δ (**3b**–EO), ppm	2.12	2.13	2.14	2.14	2.15	2.16	2.16

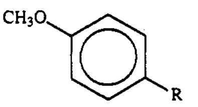
[a] The percentage of bonded EO at different temperatures has been calculated by the formula [δ(free EO) − δ(*T*)]/[δ(free EO) − δ(bonded EO)]. The EO resonance in a sample with a lithium/EO ratio of 20/1 at a temperature of 183 K has been taken as an approximation for the chemical shift of bonded EO: δ(bonded EO) = 1.29 ppm. The EO resonance in a sample with a lithium/EO ratio of 1/10 at a temperature of 333 K has been taken as an approximation for the chemical shift of free EO: δ(free EO) = 2.21 ppm. [b] Measurements at low temperatures gave complications due to the limited solubility of **3b** in toluene.

reasonable since EO is a better Lewis base than THF.[5a]

During a comparative study of the reactivities of lithium compounds in benzene or toluene toward epoxides we found that 1-lithio-2-methoxybenzene (**1b**) reacts much slower than phenyllithium and 1-lithio-4-methoxybenzene (**2b**). Whereas phenyllithium and **2b** reacted smoothly with EO at 10–20 °C, heating to 70–80 °C was necessary to initiate the reaction of **1b** with EO. This low reactivity of **1b** compared to that of **2b** is probably the consequence of the stabilizing ortho substituent in **1b**.[6] The relative low reactivity, together with our knowledge of structures of the latter compound in the presence of various ligands,[7,8] encouraged us to attempt the isolation of possibly existing coordination complexes of **1b** with epoxides. To our knowledge such intermediates have never been investigated before.



1a, R = H
b, R = Li
c, R = CH_2CH_2OH
d, R = $CH{=}CH_2$



2a, R = H
b, R = Li
c, R = CH_2CH_2OH
d, R = $CH{=}CH_2$

Results and Discussion

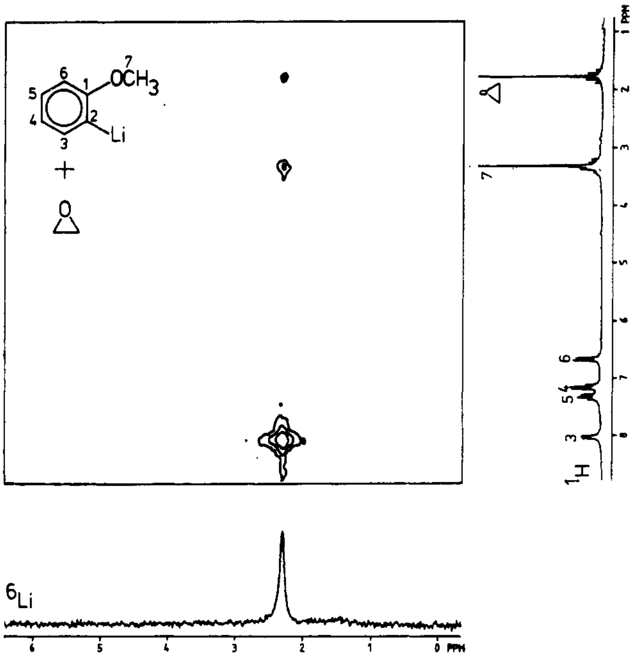
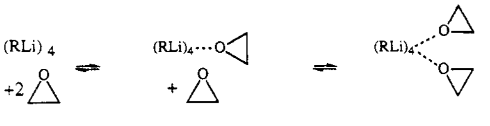


Figure 1. ^{6}Li–^{1}H HOESY spectrum of tetrakis(1-lithio-2-methoxybenzene)–bis(ethylene oxide) dissolved in benzene-d_6; contour plot; *T* = 293 K; sample enriched with 96% ^{6}Li; ^{6}Li resonance at 2.28 ppm; mixing time 2.0 s.

Crystals with the composition tetrakis(1-lithio-2-methoxybenzene)–bis(ethylene oxide) were isolated as follows. Two equivalents of EO was added to a suspension of **1b** in hexane at room temperature. The lithium compound dissolved, and immediately a new suspension was formed by precipitation of the EO coordination complex. This precipitate was dissolved by adding some toluene to the hexane suspension, and slow cooling of the resulting solution yielded well-defined single crystals. The lithium/EO ratio was found to be 2/1 by ^{1}H NMR spectroscopy. The crystals start to melt at 40–50 °C and subsequently decompose violently. The low-temperature ^{13}C NMR spectrum of these crystals (96% enriched with ^{6}Li) dissolved in toluene shows a seven-line pattern for the lithiated carbon atom (relative intensities 1/3/6/7/6/3/1; $J_{^{13}C-^{6}Li}$ = 4.9 Hz), indicating a carbon bonded to three ^{6}Li nuclei. The ^{1}H NMR spectrum at room temperature shows only one EO signal at 1.66 ppm. Since the resonance of free EO in toluene appears at 2.25 ppm, it may be concluded that in solution EO is coordinating to lithium.[9] The chemical shift of the EO proton resonance shifts downfield when the EO/lithium ratio and/or temperature are increased. This temperature dependence (Table I) suggests the presence of the equilibria shown in eq. 3. The presence of only one EO resonance (even at −90 °C) and its chemical shift dependence on the EO/lithium ratio indicate a fast-exchange process between free EO and lithium-bound EO. The ^{6}Li–^{1}H HOESY spectrum (Figure 1) of the complex shows a strong NOE between lithium and the ortho proton and small NOE's resulting from short (<3.5 Å) OCH_3···Li and EO···Li contacts, which are further evidence for EO–lithium coordination. When a toluene solution containing **1b** and EO (ratio 1/2) was heated, a decomposition reaction started at 70–80 °C. Analysis of



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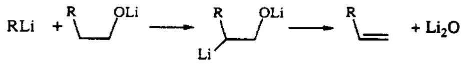
(9) Although the origin of this downfield shift is unclear, we suggest the shielding cones of the methoxyphenyl rings are responsible for this phenomenon.

Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters (Esd's in Parentheses) for Tetrakis(1-lithio-2-methoxybenzene)–Bis(propylene oxide)

atom	*x*	*y*	*z*	*U*(eq), Å^2
O(1)	0.4433 (3)	0.3390 (3)	0.5909 (3)	0.033 (1)
C(11)	0.4005 (4)	0.2919 (3)	0.6855 (4)	0.027 (2)
C(12)	0.4875 (4)	0.2495 (3)	0.7475 (4)	0.025 (2)
C(13)	0.4437 (4)	0.2048 (4)	0.8427 (4)	0.031 (2)
C(14)	0.3249 (5)	0.2009 (4)	0.8720 (5)	0.041 (2)
C(15)	0.2448 (5)	0.2425 (4)	0.8048 (5)	0.043 (2)
C(16)	0.2821 (4)	0.2880 (4)	0.7092 (4)	0.037 (2)
C(17)	0.3676 (5)	0.3988 (5)	0.5290 (5)	0.057 (2)
Li(1)	0.6629 (7)	0.3440 (6)	0.8269 (6)	0.031 (3)
O(2)	0.9109 (3)	0.4447 (3)	0.6664 (3)	0.038 (1)
C(21)	0.8340 (4)	0.5231 (4)	0.7007 (4)	0.030 (2)
C(22)	0.7187 (4)	0.4731 (4)	0.7133 (4)	0.030 (2)
C(23)	0.6431 (5)	0.5514 (4)	0.7481 (4)	0.043 (2)
C(24)	0.6795 (6)	0.6667 (5)	0.7678 (6)	0.070 (3)
C(25)	0.7942 (6)	0.7085 (5)	0.7527 (6)	0.064 (2)
C(26)	0.8754 (5)	0.6374 (4)	0.7186 (4)	0.044 (2)
C(27)	1.0316 (5)	0.4854 (5)	0.6549 (8)	0.094 (4)
Li(2)	0.6110 (7)	0.3295 (6)	0.6206 (6)	0.029 (2)
O(3)	0.6366 (3)	0.0297 (2)	0.5766 (2)	0.026 (1)
C(31)	0.6782 (4)	0.0943 (4)	0.4916 (4)	0.025 (2)
C(32)	0.7069 (4)	0.2085 (4)	0.5290 (4)	0.025 (1)
C(33)	0.7472 (4)	0.2734 (4)	0.4441 (4)	0.032 (2)
C(34)	0.7588 (4)	0.2286 (4)	0.3348 (4)	0.040 (2)
C(35)	0.7274 (5)	0.1146 (5)	0.3053 (4)	0.042 (2)
C(36)	0.6866 (4)	0.0451 (4)	0.3849 (4)	0.029 (2)
C(37)	0.6220 (4)	−0.0903 (3)	0.5556 (4)	0.032 (2)
Li(3)	0.8347 (7)	0.2882 (6)	0.6752 (6)	0.029 (2)
O(4)	0.6628 (3)	0.0565 (3)	0.8294 (3)	0.037 (1)
C(41)	0.7616 (4)	0.1224 (4)	0.8876 (4)	0.035 (2)
C(42)	0.7953 (4)	0.2234 (4)	0.8417 (4)	0.030 (2)
C(43)	0.8955 (4)	0.2872 (5)	0.8975 (4)	0.042 (2)
C(44)	0.9560 (5)	0.2552 (6)	0.9896 (5)	0.055 (2)
C(45)	0.9151 (5)	0.1542 (6)	1.0293 (5)	0.057 (2)
C(46)	0.8173 (5)	0.0861 (5)	0.9795 (4)	0.044 (2)
C(47)	0.6104 (5)	−0.0417 (4)	0.8746 (4)	0.045 (2)
Li(4)	0.6351 (7)	0.1457 (6)	0.7048 (6)	0.028 (2)
O(5)	0.0239 (3)	0.7939 (2)	0.3546 (3)	0.040 (1)
C(51)	0.0054 (4)	0.8647 (4)	0.4540 (3)	0.045 (2)
C(521)^a	0.0580 (5)	0.9157 (4)	0.3572 (4)	0.042 (1)
C(531)^a	−0.0080 (6)	0.9736 (5)	0.2758 (5)	0.042 (1)
C(522)^b	0.027 (1)	0.1020 (7)	0.6543 (7)	0.042 (1)
C(532)^b	−0.055 (2)	0.011 (1)	0.700 (1)	0.042 (1)
O(61)^c	0.3808 (6)	0.5999 (5)	0.0256 (5)	0.063 (1)
C(611)^c	0.3546 (8)	0.6412 (6)	−0.0807 (6)	0.063 (1)
C(621)^c	0.3218 (6)	0.5225 (6)	−0.0648 (6)	0.063 (1)
C(631)^c	0.1971 (6)	0.4761 (7)	−0.0420 (8)	0.063 (1)
O(62)^d	0.367 (1)	0.555 (1)	0.0502 (8)	0.063 (1)
C(612)^d	0.277 (1)	0.467 (1)	−0.001 (1)	0.063 (1)
C(622)^d	0.369 (1)	0.520 (1)	−0.0675 (9)	0.063 (1)
C(632)^d	0.344 (2)	0.608 (1)	−0.142 (1)	0.063 (1)

[a] sof = 0.78 (sof = site occupation factor). [b] sof = 0.22. [c] sof = 0.67. [d] sof = 0.33.

the products of this decomposition followed by hydrolysis gave the following: methoxybenzene (**1a**) 18%; 2-(2-methoxyphenyl)ethanol (**1c**) 78%; 2-methoxystyrene (**1d**) 4%. The formation of 2-methoxystyrene (**1d**) may be rationalized by metalation of the lithium salt of alcohol **1c** followed by Li_2O elimination (eq 4), which is likely to



(4)

proceed under the given reaction conditions. A similar reaction of **2b** with EO in toluene at much lower temperature (10–20 °C) gives only traces of product **2d**. Products after hydrolysis are as follows: methoxybenzene (**2a**), <1%; 2-(4-methoxyphenyl)ethanol (**2c**), >98%; 4-methoxystyrene (**2d**), <1%.

Table III. Bond Distances (Å) and Angles (deg) for Tetrakis(1-lithio-2-methoxybenzene)–Bis(propylene oxide)

	X^a			
	1	2	3	4
C(*X*1)–C(*X*2)	1.395 (6)	1.388 (7)	1.397 (7)	1.400 (7)
C(*X*2)–C(*X*3)	1.400 (7)	1.402 (7)	1.405 (7)	1.396 (7)
C(*X*3)–C(*X*4)	1.404 (7)	1.390 (8)	1.397 (7)	1.397 (8)
C(*X*4)–C(*X*5)	1.370 (8)	1.360 (9)	1.381 (8)	1.380 (9)
C(*X*5)–C(*X*6)	1.385 (7)	1.386 (9)	1.390 (7)	1.371 (8)
C(*X*6)–C(*X*1)	1.381 (6)	1.388 (7)	1.379 (7)	1.392 (7)
C(*X*1)–O(*X*)	1.402 (6)	1.412 (6)	1.409 (5)	1.406 (6)
O(*X*)–C(*X*7)	1.426 (7)	1.416 (7)	1.429 (4)	1.421 (6)
C(*X*1)–C(*X*2)–C(*X*3)	112.6 (4)	112.7 (4)	112.5 (4)	112.6 (4)
C(*X*2)–C(*X*3)–C(*X*4)	124.0 (5)	123.7 (5)	123.8 (4)	124.3 (5)
C(*X*3)–C(*X*4)–C(*C*5)	119.4 (5)	119.6 (4)	119.6 (4)	118.7 (6)
C(*X*4)–C(*X*5)–C(*X*6)	119.6 (5)	119.8 (5)	119.8 (5)	120.9 (6)
C(*X*5)–C(*X*6)–C(*X*1)	118.6 (5)	117.8 (5)	117.8 (5)	117.5 (5)
C(*X*6)–C(*X*1)–C(*X*2)	125.7 (4)	126.2 (5)	126.5 (5)	125.9 (5)
O(*X*)–C(*X*1)–C(*X*2)	113.4 (4)	113.0 (4)	112.3 (4)	112.7 (4)
O(*X*)–C(*X*1)–C(*X*6)	120.9 (4)	120.8 (4)	121.2 (4)	121.4 (4)
C(*X*7)–O(*X*)–C(*X*1)	118.8 (4)	118.1 (4)	118.5 (3)	118.5 (4)

O(5)–C(51)	1.444 (5)	O(5)–C(51)–C(521)	60.3 (3)
O(5)–C(521)	1.464 (5)	C(51)–C(521)–O(5)	58.6 (3)
C(51)–C(521)	1.485 (6)	C(521)–O(5)–C(51)	61.4 (3)
C(521)–C(531)	1.493 (8)	C(51)–C(521)–C(531)	124.9 (5)
		O(5)–C(521)–C(531)	116.2 (4)
O(5)–C(522)	1.46 (1)	O(5)–C(51)–C(522)	60.4 (4)
C(51)–C(522)	1.45 (1)	C(51)–C(522)–O(5)	59.5 (4)
C(522)–C(532)	1.50 (2)	C(522)–O(5)–C(51)	60.1 (4)
		C(51)–C(522)–C(532)	118.1 (9)
		O(5)–C(522)–C(532)	114.2 (9)
O(61)–C(611)	1.457 (9)	O(61)–C(611)–C(621)	59.4 (5)
O(61)–C(621)	1.447 (9)	C(611)–C(621)–O(61)	60.1 (5)
C(611)–C(621)	1.46 (1)	C(621)–O(61)–C(611)	60.5 (5)
C(621)–C(631)	1.50 (1)	C(611)–C(621)–C(631)	121.7 (7)
		O(61)–C(621)–C(631)	113.3 (6)
O(62)–C(612)	1.45 (2)	O(62)–C(612)–C(622)	59.5 (8)
O(62)–C(622)	1.45 (1)	C(612)–C(622)–O(62)	59.8 (9)
C(612)–C(622)	1.46 (2)	C(622)–O(62)–C(612)	60.6 (9)
C(622)–C(632)	1.50 (2)	C(612)–C(622)–C(632)	121.9 (9)
		O(62)–C(622)–C(632)	114.5 (9)

[a] *X* indicates the molecule number as is shown in Figure 2.

Crystals of tetrakis(1-lithio-2-methoxybenzene)–bis(propylene oxide) were prepared as described above for the EO analogue. They start to melt at 70–80 °C and then decompose violently. A NMR study of this complex in toluene shows features identical with those of the EO complex. This complex starts to decompose at 80–90 °C. Although these crystals are slightly more stable than those of the EO analogue, X-ray diffraction measurements at room temperature were not satisfying, since the crystal slowly decomposed by radiation. Attempts to solve the structure with these data were unsuccessful. The measurements were therefore carried out at 100 K.

The crystal structure of tetrakis(1-lithio-2-methoxybenzene)–bis(propylene oxide) is depicted in Figure 2. Fractional coordinates of the non-hydrogen atoms and their overall isotropic temperature parameters are given in Table II. Bond distances and angles and the lithium coordination geometry are given in Tables III and IV, respectively. The solid-state structure of this complex consists of aggregates built up from four 1-lithio-2-methoxybenzene molecules that are isostructural with the tetrameric aggregates found in tetrakis(1-lithio-2-methoxybenzene)[8] and octakis(1-lithio-2-methoxybenzene)–*N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[7] The core of the tetramer consists of a slightly distorted tetrahedron of lithium atoms, indicated by black contacts. The ipso carbon atoms of the methoxyphenyl groups are multicenter-bonded to these lithium atoms. C(12) is bound in a regular four-

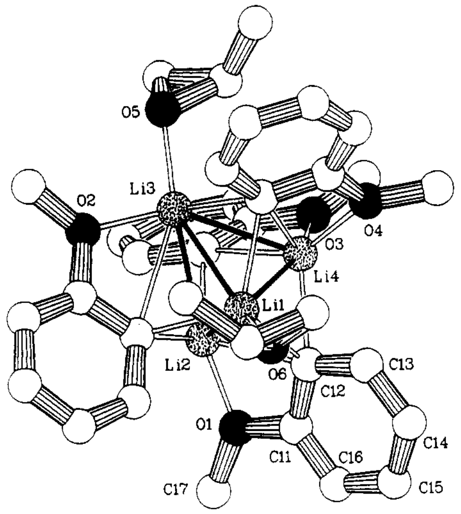


Figure 2. Perspective view of the tetrameric aggregate of tetrakis(1-lithio-2-methoxybenzene)–bis(propylene oxide). The model with the highest occupation is shown for both disordered propylene oxide molecules. Lithium atoms are indicated by speckled spheres and the oxygen atoms by black spheres; hydrogens have been omitted for clarity. The atom numbering is shown for molecule 1; the first number gives the molecule number and the second the atom number.

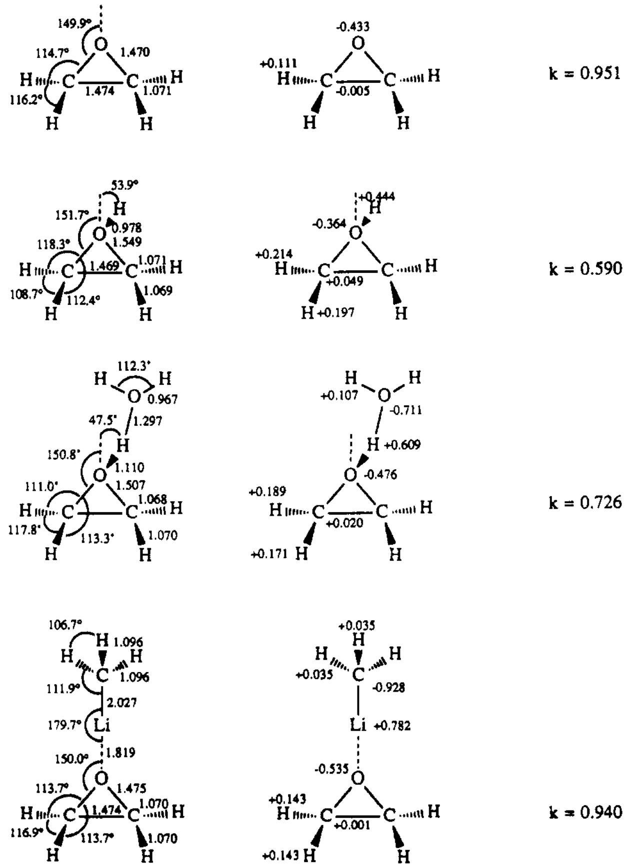


Figure 3. Optimized (ab initio, RHF, SV 3-21G) geometries for ethylene oxide (C_{2v}) the oxonium cation (C_s), the hydrated oxonium cation (C_s), and the methyllithium–ethylene oxide complex (C_s). The atomic charges (au) are given in the second column, and the third column shows the force constants for the C–O bonds (in hartree/Å^2).

Table IV. Lithium Coordination Geometry[a]

Li(1)-C(12)	2.285 (9)	Li(2)-C(12)	2.314 (9)
Li(1)-C(22)	2.221 (9)	Li(2)-C(22)	2.169 (9)
Li(1)-C(42)	2.236 (9)	Li(2)-C(32)	2.176 (9)
Li(1)-O(61)	1.95 (1)	Li(2)-O(1)	1.943 (9)
Li(1)-O(62)	1.90 (1)		
Li(3)-C(32)	2.292 (9)	Li(4)-C(12)	2.264 (9)
Li(3)-C(42)	2.270 (9)	Li(4)-C(42)	2.436 (9)
Li(3)-C(22)	2.742 (9)	Li(4)-C(32)	2.460 (9)
Li(3)-O(2)	1.983 (8)	Li(4)-O(3)	1.986 (8)
Li(3)-O(5)	2.019 (8)	Li(4)-O(4)	1.972 (8)
C(12)-Li(1)-C(22)	104.9 (3)	C(12)-Li(2)-C(22)	105.6 (3)
C(12)-Li(1)-C(42)	109.5 (3)	C(12)-Li(2)-C(32)	113.0 (3)
C(12)-Li(1)-O(61)	103.1 (4)	C(12)-Li(2)-O(1)	65.9 (3)
C(12)-Li(1)-O(62)	110.1 (6)	C(22)-Li(2)-C(32)	116.4 (4)
C(22)-Li(1)-C(42)	112.3 (4)	C(22)-Li(2)-O(1)	117.8 (4)
C(22)-Li(1)-O(61)	116.3 (4)	C(32)-Li(2)-O(1)	123.4 (4)
C(22)-Li(1)-O(62)	97.2 (5)		
C(42)-Li(1)-O(61)	110.1 (4)		
C(42)-Li(1)-O(62)	121.3 (5)		
C(32)-Li(3)-C(42)	115.4 (4)	C(12)-Li(4)-C(42)	103.5 (3)
C(32)-Li(3)-C(22)	93.9 (3)	C(12)-Li(4)-C(32)	104.8 (3)
C(32)-Li(3)-O(2)	116.7 (4)	C(12)-Li(4)-O(3)	127.4 (4)
C(32)-Li(3)-O(5)	100.4 (3)	C(12)-Li(4)-O(4)	108.4 (4)
C(42)-Li(3)-C(22)	94.7 (3)	C(42)-Li(4)-C(32)	103.9 (3)
C(42)-Li(3)-O(2)	121.1 (4)	C(42)-Li(4)-O(3)	128.9 (4)
C(42)-Li(3)-O(5)	96.7 (3)	C(42)-Li(4)-O(4)	63.0 (3)
C(22)-Li(3)-O(2)	56.5 (2)	C(32)-Li(4)-O(3)	62.2 (2)
C(22)-Li(3)-O(5)	155.7 (4)	C(32)-Li(4)-O(4)	146.3 (4)
O(2)-Li(3)-O(5)	99.3 (4)	O(3)-Li(4)-O(4)	100.5 (3)

[a] Bond distances are in Å and angles in deg.

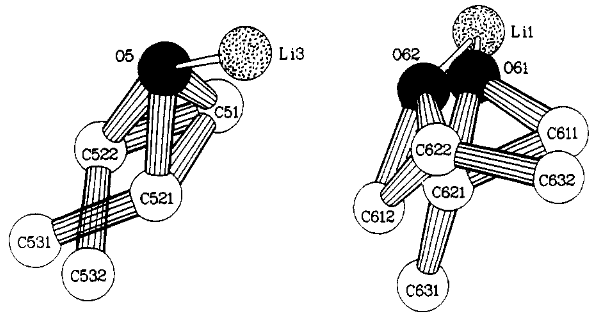


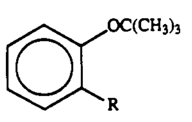
Figure 4. Perspective view of the disorder models for both propylene oxide molecules with the atom numbering. The first, second, and third numerals represent the molecule number, the atom number, and the number of the disorder model, respectively.

center–two-electron mode, whereas for C(22), C(32), and C(42) this bonding mode is distorted to a three-center–two-electron bond. This is evident from the presence of two normal C–Li bond distances and one long bond distance in the latter cases. This distortion might have something to do with O···O repulsions, since the methoxyphenyl groups concerned all possess a methoxy substituent which coordinates to a lithium that has an additional contact to another coordinating oxygen. This is confirmed by the short interatomic distances O(3)···O(4) and O(2)···O(5), which are 3.043 (4) and 3.049 (4) Å, respectively. The intramolecularly coordinating methoxy groups show O–Li bond distances in the normal range of 1.943 (9)–1.982 (8) Å. The intramolecular coordination of the methoxy groups is similar to that found in tetrakis(1-lithio-2-methoxybenzene)[8] and octakis(1-lithio-2-methoxybenzene)-*N*,*N*,*N'*,*N'*-tetramethylethylenediamine[7] and results in a propeller-like structure. This propeller arrangement seems to be typical for 1-lithio-2-methoxybenzene and its coordination complexes and is probably favored for steric reasons. The structure we suggested for tetrakis(1-lithio-2-methoxybenzene)–bis(tetrahydrofuran)[8] is therefore wrong, and apparently its structure in the solid state is isostructural with tetrakis(1-lithio-2-methoxybenzene)–bis(propylene oxide).

The propylene oxide molecules are bound to Li(1) and Li(3) with Li–O bond distances in the normal range. Unfortunately both propylene oxide molecules are disordered over several positions (Figure 4), and the structure determination has been done with geometry restraints on this molecule. Therefore, no accurate information is obtained on the geometry of the lithium-coordinated propylene oxide, which is expected to differ slightly from that of free propylene oxide; the C–O bond distance in the latter will be somewhat shorter compared to the bond distance in the lithium-coordinated propylene oxide.

In order to determine the influence of lithium–epoxide complexation upon CO bond activation, some ab initio calculations (Figure 3) have been done. The geometries of EO (C_{2v}), the oxonium cation (C_s), the hydrated oxonium cation (C_s), and the methyllithium–ethylene oxide complex (C_s) were optimized with the basis SV 3-21G. The oxonium cation has been included in the calculations since it is known to be the reactive species in the acid-catalyzed nucleophilic ring opening of epoxides[2,3] and enables a comparison to be made between the extent of activation in this system and that in the MeLi·EO complex. However, since acid-catalyzed ring-opening reactions proceed in general in aqueous solution,[10] the hydrated oxonium cation is a better model. The CO bond lengths increase in the order EO < MeLi·EO ≪ hydrated oxonium cation ≪ oxonium ion. The force constants of these CO bonds, which were determined by stretching and compressing the bonds for 0.01 and 0.02 Å while the rest of the structure was optimized, decrease in this same order. These results show only a negligible CO bond activation in the MeLi·EO complex when compared to the activation found for the oxonium cation and its hydrate. Since the electronic charge on the epoxide carbon atom determines the ease of attack by a nucleophile, charges were calculated by using the "distributed multipole analysis",[11] which gives more convincing charges than the crude Mulliken population analyses. A decrease in electron density on the epoxide carbon atom was found in the order EO > MeLi·EO ≫ hydrated oxonium cation ≫ oxonium cation, again indicating only a very small activation of the lithium-complexed epoxide ring for nucleophilic attack. The question of whether the ring-opening reaction proceeds via an organolithium–epoxide complex still remains open.

As a further experiment we tried to isolate epoxide complexes with the more sterically hindered tetrameric (cryoscopy in benzene: $n = 3.98$; $c = 0.137$ m*m*) 1-lithio-2-*tert*-butoxybenzene (**3b**). Efforts to isolate a crystalline complex of **3b** with EO failed, and only crystals of the uncomplexed compound were isolated. A 2/1 mixture of **3b** with EO dissolved in toluene shows a very small downfield chemical shift of the EO resonance in the ^{1}H spectrum, and its temperature dependence is negligible (Table I), suggesting that there is hardly any or no coordination of the EO to lithium. Probably the steric bulk of the *tert*-butoxy substituent prevents the double intramolecular coordination of these substituents to one single lithium atom, which would leave open a place for EO coordination. A reaction was started by heating a sample of **3b**–EO (1/1) to 90–100 °C, and after hydrolysis the following products were found: *tert*-butoxybenzene (**3a**), 48%; 2-(2-*tert*-butoxyphenyl)ethanol (**3c**) 26%; 2-*tert*-butoxystyrene (**3d**), 26%. The high initiation temperature, the small yield of product (**3c**), and the relatively high yield of the byproduct **3d** indicate that β-hydroxyalkylation is very slow. This experiment indicates the importance of EO–lithium coordination in the nucleophilic ring-opening reaction, but it does not prove that such a reaction must necessarily proceed via a lithium–EO complex.



3a, R = H
b, R = Li
c, R = CH_2CH_2OH
d, R = $CH{=}CH_2$

Experimental Section

General Procedures. All experiments were carried out under an inert nitrogen atmosphere with use of Schlenk techniques and syringes. Solvents were freshly distilled from sodium/benzophenone prior to use. Elemental analyses of the organolithium complexes were not attempted in view of their extreme sensitivity and their thermal decomposition. These compounds have been fully characterized by association measurements (cryoscopy), NMR spectroscopy, and X-ray analyses (when appropriate). NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H frequency 200 MHz). Deuterated solvents were dried over sodium sand and kept under nitrogen. Chemical shifts for ^{13}C and ^{1}H spectra are given with respect to TMS; chemical shifts for ^{6}Li spectra are given with respect to 1 M LiBr in THF at room temperature. Organolithium compounds were enriched with 95% ^{6}Li according to the literature.[12] Ab initio calculations were carried out by using the program GAMESS.[13] All geometries corresponding to the stationary points on the potential energy surface were located by spin-restricted Hartree–Fock (RHF) calculations with use of the SV 3-21G basis set,[14] which is a suitable minimal basis for organolithium compounds.[15] Average and maximum gradients of 0.0005 and 0.00075, respectively, were taken as the convergence criteria.

Synthesis of 1-Lithio-2-methoxybenzene (1b). One equivalent of butyllithium (3.3 mL, 1.6 M in hexane) is added to a stirred solution of 1.0 g (5.3 mmol) of 1-bromo-2-methoxybenzene in ca. 10 mL of pentane at room temperature. After a few seconds colorless crystals grow at the surface of the solution and precipitate. These crystals are washed twice with ca. 10 mL of pentane and dried in vacuo; yield 0.5 g 85%. NMR in benzene-d_6 (ppm): ^{1}H, 3.08 (OCH_3), 6.51 (d, J = 8.0 Hz), 7.24 (t, J = 7.2 Hz), 7.07 (t, J = 6.3 Hz), 7.86 (d, J = 6.3 Hz); ^{13}C, 54.1 (OCH_3), 107.0, 129.1, 122.3, 141.6, 155.9, 169.8 (aromatic resonances).

Synthesis of 1-Lithio-4-methoxybenzene (2b). One equivalent of butyllithium (5.0 mL, 1.6 M in hexane) is added to a stirred solution of 1.5 g (8.1 mmol) of 4-bromo-2-methoxybenzene in ca. 10 mL of pentane at room temperature. After 2 h the fine colorless precipitate is isolated and washed twice with ca. 10 mL of pentane and dried in vacuo; yield 0.8 g, 89%. NMR of this compound with 2 mol equiv of THF in toluene-d_8 (ppm): ^{1}H, 1.18 and 3.18 (THF), 3.52 (OCH_3), 7.00 (d, J = 8.0 Hz), 8.15 (d, J = 8.0 Hz); ^{13}C, 33.6 and 68.0 (THF), 54.3 (OCH_3), 113.1, 142.0, 159.2, 162.5 (aromatic resonances).

Synthesis of 1-Lithio-2-*tert*-butoxybenzene (3b). One equivalent of butyllithium (8.3 mL, 1.6 M in hexane) is added to a solution of 2.0 g (13.3 mmol) of *tert*-butoxybenzene (**3a**) and 2 mol equivalents of tmeda (4.0 mL) in ca. 30 mL of hexane. The temperature is raised to +50 °C, and after 1 h the solution is slowly cooled to room temperature, resulting in the precipitation of good colorless crystals in which tmeda is included. The crystals are isolated, washed twice with pentane, and dried in vacuo; yield 1.29 g 62%. NMR in benzene-d_6 (ppm): ^{1}H, 1.07 (O*t*Bu), 6.84

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(d, J = 7.9 Hz), 7.07 (t, J = 6.6 Hz), 7.19 (t, J = 7.3 Hz), 8.11 (d, J = 6.5 Hz); ^{13}C, 28.5 and 77.1 (O*t*Bu), 112.9, 122.9, 128.3, 141.6, 159.1, 167.3 (aromatic resonances).

X-ray Determination. Propylene oxide (0.8 mL; 11.4 mmol) was added to a suspension of **1b** (0.66 g, 5.8 mmol) in ca. 7 mL of hexane. The lithium compound dissolves immediately, and a new precipitate of tetrakis(1-lithio-2-methoxybenzene)–bis(propylene oxide) is formed. Toluene is added until most of the precipitate is dissolved. The solution is separated from the remaining solid, and slow cooling to −30 °C yields good-quality crystals. The 1-lithio-2-methoxybenzene/propylene oxide ratio of 2/1 was determined by ^{1}H NMR spectroscopy. A rod-shaped crystal (1.5 × 0.5 × 0.3 mm) was covered under nitrogen with very pure paraffin and mounted on a Lindemann glass capillary. Data were collected at 100 K on an Enraf-Nonius CAD-4F diffractometer with Zr-filtered Mo Kα radiation. Cell parameters were determined by means of the SET4 method[16] from 25 reflections with $12.5 < \theta < 19.3°$. The crystal system is triclinic with cell parameters a = 11.348 (1) Å, b = 12.043 (1) Å, c = 12.099 (1) Å, α = 95.57 (1)°, β = 92.30 (1)°, and γ = 97.52 (1)°. The intensity data of 4816 unique reflections were collected within half of the reflection sphere ($0 \le h \le 13$, $-14 \le k \le 14$, and $-14 \le l \le 14$) with $2\theta_{max}$ = 48.4°. The scan mode was ω–2θ with $\Delta\omega = (0.7 + 0.35 \tan \theta)°$. Three reference reflections (1,0,−3; 120; 022) were measured every 30 min and showed no significant variation (ca. 2% decay). After correction for polarization and Lorentz effects 3216 reflections survived for which $I \ge 2.5\sigma(I)$.

On the basis of Wilson statistics, the space group was assumed to be $P\bar{1}$, and this was later confirmed by refinement in this space group. The structure was solved by using direct methods (SHELXS-86)[17] and subsequent Fourier analysis. Hydrogen atoms were placed at calculated sp^2 and sp^3 positions (C–H = 1.00 Å). During the refinement, high isotropic temperature parameters for the propylene oxide molecules together with some rest electron density around these molecules indicated disorder. A model for the disorder (Figure 4) was found by treating the propylene oxide geometry as a rigid body with some flexibility. The geometry of the rigid body was taken from the gas-phase structure of propylene oxide obtained by electron diffraction.[18] The following bond distances (Å) were fixed: O–C = 1.450 ± 0.005; CH_2–$CHCH_3$ = 1.464 ± 0.005; C–CH_3 = 1.500 ± 0.005; C–H = 1.000 ± 0.001. Angles were set by fixing the following nonbonding distances (Å): $CH_2 \cdots CH_3$ = 2.60 ± 0.01; O···CH_3 = 2.49 ± 0.01; O···H = 2.05 [illegible] 0.01; H···$CHCH_3$ and H···CH_2 = 2.14 ± 0.01. The hydrogens of the methyl group were placed on ideal calculated sp^3 positions (C–H = 1.00 Å). A difference Fourier determination on this rigid propylene oxide molecule with an occupation of 0.70 resulted in electron density maxima from which the disorder model was constructed. Full-matrix least-squares refinement on this structure, including the restrained propylene oxide models, converged to $R(F)$ = 0.073 with a mean shift/error ratio of 0.001. Since some rest electron density of 0.79 electron is found in the vicinity of the disorder models for propylene oxide, these models do not give a complete description of the disorder. Most likely these molecules are disordered over several other positions with low occupation. The methoxy group carbon C(27) displays a rather high anisotropic temperature factor (0.21 Å^2) perpendicular to the phenyl ring plane. Since the C(27)···O(5) distance is short (3.330 (7) Å), this is presumably due to disorder, which correlates with the disorder found for the propylene oxide molecule 5.

The scattering factors for non-hydrogen atoms were taken from Cromer and Mann[19] and those for hydrogen atoms from Stewart, Davidson, and Simpson.[20] Anomalous dispersion factors were taken from Cromer and Liberman.[21] Calculations were performed on a MicroVAX-II computer using the programs SHELXS-89[17] (structure determination), SHELX-76[22] (refinement), and the EUCLID package (geometric calculations and graphics).[23]

Acknowledgment. Ab initio calculations were performed on the CYBER 205 computer of SARA (Amsterdam). We thank the Dutch Supercomputing Working group (WGS) for an allowance of computer time.

Supplementary Material Available: Listings of thermal parameters for the non-hydrogen atoms and positional parameters and isotropic thermal parameters for the hydrogen atoms (2 pages); a listing of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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