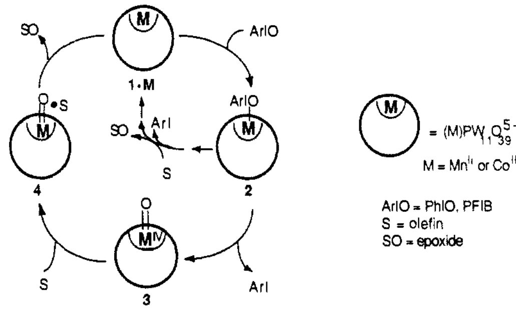
Scheme I



in Table I; exact reaction conditions are given in the table.[18] The following points pertain to all reactions catalyzed by **1**-M: (1) no reaction is seen in the absence of either **1**-M or oxidant; (2) the reactivity order for **1**-M is M = Mn^{II} and Co^{II} (most reactive) > Cu^{II} > Fe^{II} ~ Cr^{III} (almost inactive at 25 °C); (3) *trans*-stilbene gives *trans*-stilbene oxide and benzaldehyde only (6:1 mol ratio); *cis*-stilbene gives partially isomerized olefin, *cis*- and *trans*-epoxides, and benzaldehyde, products compatible with one or more freely rotating radical intermediates; (4) the selectivity for production of epoxide is higher in the reactions catalyzed by **1**-M than in the reactions catalyzed by the metal triflates or metalloporphyrins (>90% for **1**-M with all olefins examined);[18] (5) intermediate alkyl radicals are sufficiently long-lived and kinetically accessible to be scavenged by any dioxygen purposely added to the system producing typical autoxidation products (primarily allylic alcohol and allylic ketone vs. epoxide) but not by alkylated phenols, e.g., BHT; (6) the rates of epoxidation with PFIB, chosen as oxygen donor for its reactivity, follow the order **1**-Co and **1**-Mn (most reactive) ≥ FeTDCPPCl > MTPPCl > $M(OTf)_2$,[19] M = Fe^{III} or Mn^{III}; (7) most importantly, epoxidations catalyzed by **1**-M continue far longer than for all other systems examined. Several epoxidations with all the catalysts in Table I and PFIB were examined under high turnover conditions (10 000 equiv of PFIB per equiv of catalyst). The stability order of these homogeneous catalysts, monitored by both the spectral properties of the catalysts and the rate of PFIB uptake with time, is clear: $M(OTf)_2$ (least stable) < MTPPCl, M = Fe^{III} or Mn^{III}, ≪ FeTDCPPCl < **1**-M, M = Co^{II} or Mn^{II} (most stable). Only the catalysts, **1**-M, appear to be oxidatively stable in the absence of olefin substrate.

It is clear from monitoring the electronic spectra of the epoxidations catalyzed by **1**-Co or **1**-Mn that the Mn ion undergoes redox changes during catalysis, while the Co atom may not. These observations coupled with the known difficulty of obtaining Co in the 4+ oxidation state favors paths involving high-valent Mn species (e.g., oxomanganese (IV), **3** in Scheme I) in the processes catalyzed by **1**-Mn but paths not involving oxocobalt species (i.e., **1**-M → **2** → **1**-M in Scheme I) in the processes catalyzed by **1**-Co.

Studies are in progress that address the energetic and mechanistic features of these sustained epoxidation processes. At this stage it is apparent that **1**-M and related species may combine the stability of heterogeneous inorganic oxidation catalysts such as metal oxides with the experimental tractability of homogeneous oxidation catalysts containing organic ligands such as metalloporphyrins.

Acknowledgment. Support of this research by the National Science Foundation (Grant CHE-8402994) is acknowledged. We thank Judy Sophianopoulos for GC/MS analyses and Michael M. Williamson for the sample of FeTDCPPCl.

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(18) Reaction rates and catalyst stabilities were monitored directly and most effectively by gravimetric analysis of unreacted iodosylarene and by gas chromatographic analysis of iodoarene. Selectivities are defined as yield of epoxide/total yields of other volatile or chromatographically detectable products. Product mixtures were not analyzed for carboxylates or other nonvolatile materials which may be present.

(19) Abbreviations in Table I.

Enthalpies of Intramolecular Etheration of Saturated Organolithium Compounds in Benzene

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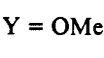
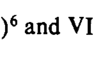
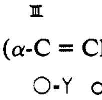
Data on alkyllithium-Lewis base (B) interaction obtained so far[1-5] pertain to *mixtures* of rapidly equilibrating complexes $R_4Li_4B_n$ (n = 1-4) and B and, consequently, depend upon concentrations and on the ratio RLi:B. For primary alkyllithiums, the gross calorimetric[3,4] and thermodynamic[5] data cannot be dissected into the separate contributions of the (free) energy of transfer of RLi from the hexameric state (predominating in hydrocarbons) to the tetrameric state (prevailing in solutions when the mole ratio of B to *n*-alkyllithium hexamer is about 1)[2b] and the (free) energy of complexation in the latter. In order to obtain data on specific complexes we have studied the lithium compounds I,[6] II,[7] III[7,8] and IV.[7] I and II crystallize as V (α-C = $CHCH_3$, Y = OMe)[6] and VI (α-C = CH_2, Y = OMe).[9] In hydrocarbon solutions VII is present as V (α-C = CH_2, Y = OMe) exclusively, as indicated by molecular weight and diastereotopic C-methyl groups and CH_2Li protons,[10] while VIII occurs as a mixture of V (α-C = CH_2, Y = NMe_2) and VI (α-C = CH_2, Y = NMe_2).[11] By analogy complexes V and/or VI most likely are the exclusive species present in hydrocarbon solutions of I-IV.[12,13] They are taken as models for corresponding, more ephemeral, intermolecular complexes $R_4Li_4(OR'_2)_4$.



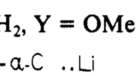
I



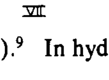
II



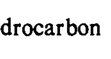
III



IV

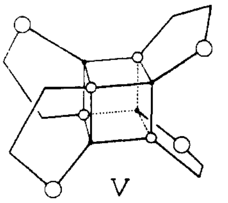


VII

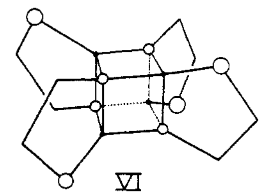


VIII

O-Y o-α-C ..Li



V



VI

Heats of reaction [$\Delta H_{r,s\text{-BuOH}}$(25 °C)] of ca. 10^{-3} M benzene solutions of I-IV and of the methoxy-free reference compounds

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(1) (a) Lindman, B.; Forsén, S. "NMR and the Periodic Table"; Harris, R. K., Mann, B. E.; Eds.; Academic Press: London, New York, San Francisco, 1978; p 166. (b) Sergutin, V. M.; Zgonnik, V. N.; Kalninsh, K. K. *J. Organomet. Chem.* **1979**, *170*, 151. (c) Waak, R.; Doran, M. A. *J. Am. Chem. Soc.* **1963**, *85*, 1651. Screttas, C. G.; Eastham, J. F. *Ibid.* **1966**, *88*, 5668. Holm, T. *Acta Chem. Scand.* (*B*) **1978**, *32*, 162.

(2) (a) West, P.; Waak, R. *J. Am. Chem. Soc.* **1967**, *89*, 4395. (b) Lewis, H. L.; Brown, T. L. *Ibid.* **1970**, *92*, 4664.

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(5) Kminek, I.; Kaspar, M.; Trekoval, J. *Collect. Czech. Chem. Commun.* **1981**, *45*, 1132.

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(7) Prepared in the same way as I.[6]

(8) (a) Boerhorst, E.; Schmitz, R. F.; Klumpp, G. W. *Tetrahedron Lett.* **1975**, 3347. (b) Boerhorst, E. Thesis, Vrije Universiteit Amsterdam, 1978.

(9) Klumpp, G. W.; Vos, M.; Spek, A. L., unpublished results.

(10) Klumpp, G. W.; Vos, M.; Dorlas, R.; de Kanter, F. J. J., unpublished results.

(11) Klumpp, G. W.; Vos, M.; de Kanter, F. J. J.; Slob, C.; Krabbendam, H.; Spek, A. L. *J. Am. Chem. Soc.*, in press.

(12) Since several diastereomeric tetramers seem to be present, unequivocal interpretation of the temperature-dependent NMR spectra of I has not yet been possible. The NMR spectra of II suggest the exclusive presence of tetramers of type VI.

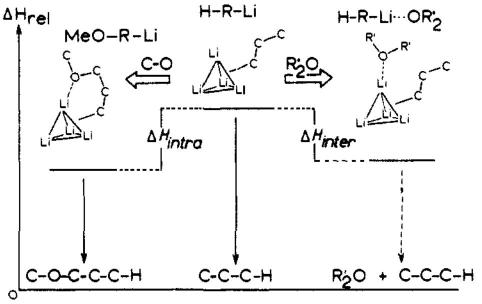

Figure 1. Relative enthalpies of formation (per mole of RLi) of tetrameric alkyllithiums and (γ-alkoxy)alkyllithiums, as determined from differences between heats of protonation (represented by solid vertical arrows). For clarity, only one (γ-alkoxy)alkyl group and one ether molecule (R'_2O) are shown.

Table I. Enthalpies of Protonation ($\Delta H_{r,ZH}$; Z = s-BuO, Br; kJ/mol of RLi, 25 °C) of Saturated Organolithium Compounds[a]

RLi	deg of assocn[b]	$\Delta H_{r,s\text{-BuOH}}$[b]	$\Delta H_{r,BrH}$[c]	$\Delta H_{r,BrH} - \Delta H_{r,s\text{-BuOH}}$
I	4[d]	−199 + 4		
II	4[e]	−190 ± 2		
III	4[e]	−199 ± 2	−333 ± 6[f]	−134
IV	4?[g]	−190 ± 3		
IX	4[h]	−240 ± 5	−374 ± 4[i]	−134
X	6[e]	−219 ± 2		
XI	6[j]	−221 ± 4	−354 ± 4[i]	−133
XII	4[e]	−222 + 5	−360 ± 9[f]	−138

[a] All operations were carried out in evacuated sealed vessels using the break seal technique. In the solutions of RLi no impurities were detectable by NMR and double titration. [b] In benzene. [c] In pentane. [d] Reference 6. [e] This work; determined by the method of ref 16. [f] Reference 8b. [g] Insufficiently soluble for measurement, presumably tetrameric. [h] Reference 17. [i] Reference 15. [j] Cf. reference 2b.

s-BuLi (IX), n-PrLi (X), n-BuLi (XI), and 2-norbornyllithium (exo:endo ca. 1, XII), respectively, with a slight excess of s-BuOH (0.2 M in benzene) were measured[14] and are given in Table I together with some earlier values [$\Delta H_{r,BrH}$(25 °C)] obtained with gaseous HBr in pentane.[8b,15]

The very similar values of $\Delta H_{r,BrH} - \Delta H_{r,s\text{-BuOH}}$ attest to the internal consistency of the two sets of data. If the same *relative enthalpy of formation in benzene* is assigned to protonation products differing only by the presence or absence of OMe at C-γ the difference between two values of ΔH_r must be ascribed to the *difference between the relative enthalpies of formation in benzene per mole of RLi* of the two lithium compounds compared. Lowerings of relative enthalpies of formation (enthalpies of intramolecular etheration, ΔH_{intra}) incurred by transformation of a "normal" organolithium compound (H–R–Li) into its γ-methoxy analogue (MeO–R–Li) are (see Table I, kJ/mol of RLi; Figure 1) −41 (IX → I), −23 (XII → III), and −30 [av X → II (or IV) and XI → II (or IV)]. The value of $|\Delta H_{intra}|$ is largest in the s-butyl system in which both H–R–Li (IX) and MeO–R–Li (I) have the same degree of aggregation. It is slightly larger than that of the "initial enthalpy of interaction" (ΔH_{inter} = −36 kJ/mol of THF) obtained for the sterically more demanding *intermolecular* formation of i-Pr_4Li_4·THF in benzene (mole ratio THF_{added}:i-PrLi = 0.08).[3] The smaller value of $|\Delta H_{intra}|$ found for the 2-norbornyl system shows that on an (*exo*-2-norbornyl)$_4Li_4$ cluster even intramolecular etheration by γ-MeO is weakened by steric crowding. For primary alkyllithiums where H–R–Li (X, XI) occurs predominantly as a hexamer and MeO–R–Li (II, IV) as a tetramer the γ-OMe-induced lowering of the relative enthalpy of formation per mole of RLi is smaller than for the s-alkyllithiums since it is the sum of opposing contributions by the enthalpy of deaggregation ($\Delta H_{6\to4}$) and ΔH_{intra} of an n-alkyllithium tetramer (eq 1).

$$\Delta H_{6\to4} + \Delta H_{intra} = -30 \text{ kJ/mol of RLi} \qquad (1)$$

Assuming that for the sterically less encumbered primary alkyllithiums ΔH_{intra} matches ΔH_{inter} more closely than found for I and i-PrLi, eq 1, with ΔH_{inter} instead of ΔH_{intra}, may be substituted into eq 3, which specifies the enthalpy changes constituting the enthalpy of etheration of n-BuLi by THF in benzene (eq 2).[4]

$$\begin{gathered} n\text{-}Bu_6Li_6 + 1.5p\text{THF} \rightleftharpoons 1.5n\text{-}Bu_4Li_4{\cdot}p\text{THF} \\ \Delta H(\text{benzene, 30 °C}) = -120 \text{ kJ/mol of } n\text{-}Bu_6Li_6 \end{gathered} \qquad (2)$$

$$-120 = 6\Delta H_{6\to4} + 1.5p\Delta H_{inter} \qquad (3)$$

$$p = \frac{60}{-45 - 1.5\Delta H_{6\to4}} + 4 \qquad (4)$$

The resulting relationship (eq 4) gives the number (p) of THF molecules bonded to one molecule of n-Bu_4Li_4 in benzene as a function of $\Delta H_{6\to4}$. Choosing values of $\Delta H_{6\to4}$ between 10 and 25 kJ/mol of RLi[18] [ΔH_{inter} (=ΔH_{intra}) = −40 to −55 kJ/mol of RLi] one obtains values of p ranging from 3.0 to 3.3 in agreement with the finding that the average number of THF molecules that can maximally be bonded to n-Bu_4Li_4 in cyclohexane is 3.6, while "the equilibria appear to proceed to a smaller extent in benzene".[2b,19]

Acknowledgment. We are grateful to Prof. Dr. F. Bickelhaupt, Dr. O. S. Akkerman, and G. Schat for making available the calorimeter developed by them and providing advice and practical help in its use.

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(13) Thermochemistry also suggests the absence of tetramers whose CH_2CH_2Y moieties are in the open-chain form. Their enthalpies of intramolecular Li···Y coordination would not differ greatly from ΔH_{intra} (vide infra). For a $\Delta H_{Li\cdots Y}$ of, say, −35 kJ/mol of RLi presence of 5% of open-chain CH_2CH_2Y requires $\Delta S_{Li\cdots Y}$ to amount to −93 J/(mol of RLi deg). This value seems unrealistic since ΔS^{*} for interchange (supposedly through ring opening–ring closure) of V and VI (Y = OMe, NMe_2) is in the range of 46 J/(mol of RLi deg).[10,11]

(14) Calorimeter: Freijee, F. J. M.; van der Wal, G.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1982**, *240*, 229.

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(18) Other values (kJ/mol of RLi) of $\Delta H_{6\to4}$: s-BuLi, 2.4 (Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255); i-PrLi, 1.7 (Sergutin, V. M.; Antonov, N. G.; Zgonnik, V. N.; Kalninsh, K. K. *J. Organomet. Chem.* **1978**, *145*, 265).

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Epoxidations of Olefins by Peroxy Intermediate Generated in Situ from CCl_4 and Superoxide[†]

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Considerable interest has been focused on the reactivities of the peroxy intermediate $Cl_3COO\cdot$,[1] which may be formed in the reaction of superoxide with CCl_4. Sawyer has reported that in aprotic solvents, superoxide (O_2^-) can oxygenate CCl_4 to yield $HOC(O)O^-$ as an overall product via formation of $Cl_3COO\cdot$ radical and Cl_3COO^- anion.[2] The initial step is believed to be some form of interaction between O_2^- and CCl_4. The resulting

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[†] This work was supported by a research grant from the Ministry of Education, Science and Culture of Japan.

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