following dimensionless formulation is obtained, noting that the steady-state approximation is applied to $HO_2^{\bullet}$ and HO_2^-

$$\frac{\partial 2a + b}{\partial \tau} = \frac{\partial^2 2a + b}{\partial y^2}, \frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \frac{2\lambda_2 b^2}{b + \dfrac{\lambda_{-2}}{\lambda_5} w}, \frac{\partial b + w}{\partial \tau} = \frac{\partial^2 b + w}{\partial y^2}$$

$$\tau = 0,\ y > 0 \text{ and } y = \infty,\ \tau > 0{:}\quad a = 1,\ b = w = 0$$

$$y = 0,\ \tau > 0{:}\quad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0,\ \frac{\partial w}{\partial y} = 0,\ a = 0$$

$$\psi = (\partial a / \partial y)_0$$

The system thus depends upon two parameters that can be chosen either as λ_2 and λ_{-2}/λ_5 or as $(\lambda_2/\lambda_{-2})\lambda_5$ and λ_{-2}/λ_5.

If $\lambda_{-2}/\lambda_5 \rightarrow 0$, the rate-determining step is reaction 2, we obtain the DISP1 behavior, and R is then a function of λ_2. Conversely, if $\lambda_{-2}/\lambda_5 \rightarrow \infty$, the rate-determining step is reaction 5, reaction 2 being a preequilibrium, we obtain the DISP2 behavior. For intermediate values of the parameter λ_{-2}/λ_5 $(=k_{-2}/k_5)$, the working curves were computed by an explicit finite difference[23] resolution of the above system. The results are shown in Figure 5 under the form of R vs. λ_2 (Figure 5a) and R vs. $\lambda_2\lambda_5/\lambda_{-2}$ (Figure 5b) working curves for a series of values of the competition parameter k_{-2}/k_5. In order to apply the finite difference technique to only the two last partial derivation equations, the first one was integrated formally leading to

$$b_0 = 2 - \pi^{-1/2} \int_0^{\tau} \psi(\eta)(\tau - \eta)^{-1/2}\, d\eta$$

Conclusions

The main conclusions emerging from the above results and discussion concern the chemical reactivity of the $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radicals generated from the electrochemical generation of the former in the presence of acids. In aprotic solvents, the $HO_2^{\bullet}$ radical appears as an electron transfer oxidant toward $O_2^{\bullet-}$ rather than an H-atom abstractor from the solvent or from another $HO_2^{\bullet}$ radical. $O_2^{\bullet-}$ displays both weak base and weak electron-transfer reductant properties. In neutral and moderately acidic media, the mechanism of superoxide ion disproportionation in aprotic solvents such as Me_2SO and DMF appears to be quite similar to what it is in water[17] involving, after protonation into the $HO_2^{\bullet}$, electron transfer to $HO_2^{\bullet}$ from $O_2^{\bullet-}$.

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Registry No. O_2, 7782-44-7; $O_2^{\bullet-}$, 11062-77-4; $HO_2^{\bullet}$, 3170-83-0; phenol, 108-95-2; *p*-cresol, 106-44-5; 4-bromophenol, 106-41-2; 4-chlorophenol, 106-48-9; 2,4-dimethylphenol, 105-67-9; nitromethane, 75-52-5.

Communications to the Editor

Isolation and X-ray Crystal Structure of the Tetrameric Lithium-Coordinated α-Sulfonimidoyl Carbanion $[(Me_3Si)CH\{S(O)(NSiMe_3)\}Li]_4$: The First Structure of an α-SO Substituted Lithium Alkyl Having No External Donor Ligands

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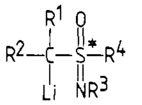
The chiral lithium alkyl sulfoximides **1** have been established as useful intermediates in asymmetric synthesis.[2] For a deeper understanding of the factors determining the reactivity of **1**, e.g., in asymmetric bond formation[2a,b] and elimination[2c] reactions, knowledge of their structure is a prerequisite. Up till 1986, however, definitive structural information about **1** was completely lacking. Recently we described an X-ray crystal structure analysis of the tetramethylethylenediamine (tmeda)-complexed (*S*)-(*N*-methyl-*S*-phenylsulfonimidoyl)methyllithium (**1a**),[3] which revealed a chiral tetramer, $(\mathbf{1a})_4\cdot(\text{tmeda})_2$, of approximately C_2 symmetry, with short bonds between the anionic C atoms and the sulfonimidoyl groups [mean value of C–S distance, 1.64 (2) Å], similar to those found in lithium alkyl sulfones,[4] and two different kinds of Li and anionic C atoms, respectively. Whereas two of the latter have a C–Li bond [mean value of C–Li distance, 2.49 (5) Å], the others are only weakly, if at all, coordinated, each to two Li atoms [mean value of C–Li distance, 3.23 (4) Å]. However, the strongly chelating tmeda ligands should undoubtedly play a significant role in the structure of $(\mathbf{1a})_4\cdot(\text{tmeda})_2$, and the alteration brought about by the donor ligands was an open question. We now report the X-ray crystal structure of the (trimethylsilyl)[*N*-(trimethylsilyl)-*S*-phenylsulfonimidoyl]methyllithium tetramer $(\mathbf{1b})_4$ having no external donor ligands and first results about its solution structure. The two trimethylsilyl groups were deliberately chosen, among other reasons, to achieve sufficient solubility of **1b** in noncomplexing solvents, allowing not only crystal growing but also NMR investigations therein. **1b** which carries two different substituents at the anionic C atom was generated from (±)-trimethyl[(*N*-(trimethylsilyl)-*S*-phenylsulfonimidoyl)methyl]silane (**2**)[5] with 1 equiv of *n*-butyllithium in *n*-hexane at -30 °C. Clear colorless crystals which are *readily soluble in cyclohexane as well as tetrahydrofuran* (THF) were slowly grown from a 4:1 cyclohexane/*n*-hexane mixture at room temperature. The X-ray



1a, $R^1 = R^2 = H, R^3 = Me, R^4 = Ph$
1b, $R^1 = H, R^2 = R^3 = SiMe_3, R^4 = Ph$

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[4] (a) $[(CH_2SO_2Ph)Li\cdot tmeda]_2$: Gais, H.-J.; Lindner, H. J.; Vollhardt, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 859. (b) $[(PhCHSO_2Ph)Li\cdot tmeda]_2$: Boche, G.; Marsch, M.; Harms, K.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 573. (c) $[(CH_2{=}CHCHSO_2Ph)Li\cdot diglyme]_2$: Gais, H.-J.; Vollhardt, J.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 939.

[5] For synthesis, see: Dingerdissen, U. Diploma Thesis, Technische Hochschule Darmstadt 1985.

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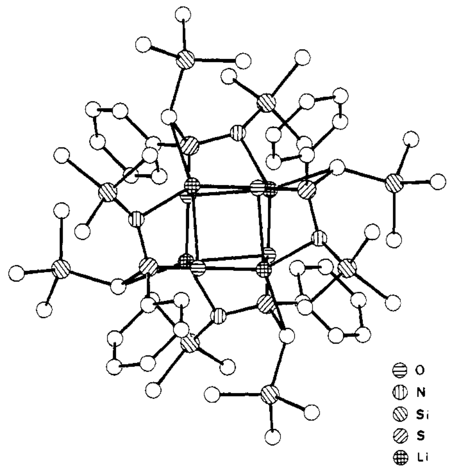

Figure 1. Molecular structure of $[(Me_3Si)CH\{S(O)(NSiMe_3)\}Li]_4$ [(**1b**)$_4$]. Selected interatomic distances (Å) and bond angles (deg): S–O 1.499 (3), S–N 1.512 (3), S–C1 1.637 (4), S–C2 1.797 (4), O–Li 2.408 (7), O–Li* 1.934 (7), O–Li** 2.097 (7), N–Li 2.113 (7), C1–Li** 2.430 (8), Li**–O–Li* 94.7 (3), Li**–O–Li 82.0 (2), Li*–O–Li 95.6 (3), Li**–C1–H1 85 (2), Li**–C1–Si1 121.8 (3), Li–C1–S 80.4 (2), H1–C1–Si1 120 (2), H1–C1–S 107 (2), Si1–C1–S 128.0 (2), C2–S–C1–Si1 −102, C2–S–C1–H1 53, N–S–C1–Si1 24, O–S–C1–H1 −58.

structure analysis[6] shows a chiral tetramer, (**1b**)$_4$, with C_2 symmetry built of two *R,R* and two *S,S* diastereomers of **1b** as depicted in Figure 1.

Four Li and four O atoms form a cubelike Li_4O_4 skeleton of edges 1.934 (7), 2.097 (7), and 2.408 (7) Å. Each Li atom attains pentacoordination through the O and C atoms of a first, the N and O atoms of a second, and the O atom of a third sulfonimidoyl carbanion. The N and C atoms of the four carbanions are anchimerically[7,3] coordinated to the Li atoms, thereby forming a chain of eight four-membered O–S–C–Li and O–S–N–Li rings alternatingly annelated to the central "cube" (Figure 2). The lattice contains also two cyclohexane solvent molecules per one (**1b**)$_4$. The ready solubility of the tetramer (**1b**)$_4$ in hydrocarbon solvents seems due to a shielding of its polar core of positively charged Li atoms and negatively charged C, N, and O atoms by the nonpolar eight trimethylsilyl and the four phenyl groups located at the surface. The coordination geometry of C1 is of particular interest. Relative to the S, Si1, and H1 atoms, C1 is pyramidalized with its deviation from the plane S–Si1–H1 being 0.17 Å. In the case of (**1a**)$_4$·(tmeda)$_2$, the configuration of C1 is uncertain, because the position of the H1 atoms could not be located with sufficient accuracy.[3] The Li**–C1–H1 [85 (2)°] and Li**–C1–S [80.4 (2)°] angles are rather small. **1b** adopts a conformation in the tetramer (**1b**)$_4$ which has the C2–S bond approximately anti to the Li**–C1 bond, the latter being placed with a bond length of 2.430 (8) Å in the upper region of C–Li bond lengths.[8]

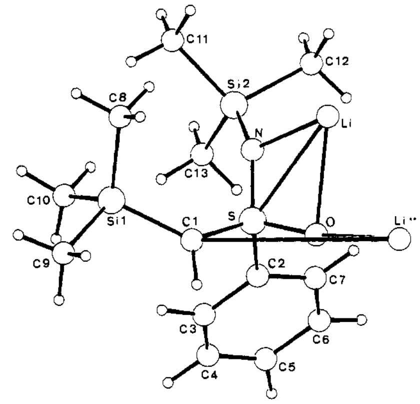

Figure 2. Partial structure of (**1b**)$_4$ showing the atom numbering scheme.

The S–C1 bond, on the other hand, has a length of 1.637 (4) Å (like the one in (**1a**)$_4$·(tmeda)$_2$) and thus considerably shortened compared to *S*-alkylsulfoximides (average value of C–S distance, 1.74 Å).[2] This could be ascribed to a similar stabilizing n_C–σ^*_{SPh} interaction as in α-sulfonyl carbanions.[4,9] In summary, it seems that the bonding situation in the tetramers (**1a**)$_4$·(tmeda)$_2$ and (**1b**)$_4$ can be best described as a mainly electrostatic interaction between Li cations and α-sulfonimidoyl carbanions having three coordination sites.

What can be said about the solution structure of **1b**, a point of special significance in regard to the reactivity of **1**?[2] The ^{13}C NMR spectrum[10] of the species obtained by dissolving crystalline (**1b**)$_4$ in cyclohexane-d_{12} at room temperature shows the signal for C1 as a broad doublet at 36.4 ppm shifted upfield as expected by 16.5 ppm relative to the parent compound **2**. More revealing, however, is the low $\Delta^1J(^{13}C,^1H)$ value of 5 Hz for C1 on going from **2** to **1b**, strongly indicating[4c,11] also for the species in cyclohexane solution, which should be close in its structure to that of (**1b**)$_4$, a hybridization at C1 between sp^3 and sp^2. On changing the solvent from nonsolvating cyclohexane to strongly solvating THF, one observes the ^{13}C NMR signal of C1 slightly downfield as a doublet at 40.6 ppm but now showing a much larger Δ^1J($^{13}C,^1H$) value of 15.0 Hz for C1. This points to the formation of a new THF-solvated aggregate with a more flattened C1 atom having less or even no C–Li contact. Further investigations to establish the solution structure of **1**[3] by ^{13}C and ^6Li NMR spectroscopy are under way.

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Registry No. **1b**, 108083-29-0; (**1b**)$_4$·$2C_6H_{12}$, 108083-30-3; **2**, 108083-31-4; *n*-butyllithium, 109-72-8.

Supplementary Material Available: Tables and computer printout giving crystal data and details of data collection, atomic coordinates, thermal parameters, and interatomic distances (4 pages); table of structure factors (13 pages). Ordering information is given on any current masthead page.

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(6) (a) Experimental data: $(C_{13}H_{24}LiNOSSi_2)_4 \cdot 2C_6H_{12}$, $M_w = 1390.4$ g/mol, $a = 18.100$ (3) Å, $b = 18.100$ (3) Å, $c = 13.024$ (2) Å, $\alpha = \beta = \gamma = 90°$, $V = 4266.7$ Å^3, $T = 220$ K, $\rho_c = 1.08$ g/cm^3, $Z = 8$, $\mu_{(Mo)} = 2.55$ cm^{-1} (no absorption correction), $\lambda = 0.71069$ Å, space group $P\bar{4}2c$ (*no.* 114), total number of reflections 18 194 ($\pm h \pm k + l$), number of independent reflections 4134 ($R_{av} = 0.019$), number of observed reflections 3610, number of refined parameters 204, $R = 0.054$, $R_w = 0.055$ ($w = 1/\sigma^2(F_o)$), final difference fourier ≤ 0.52 e/Å^3; hydrogen atom positions of the tetramer have been determined by difference fourier methods, but only atom H1 has been refined; no hydrogen atoms have been included for the solvent molecule because of disorder problems in the carbon skeleton. (b) Computations were done on VAX-11/780, VAX-11/730, and MicroVAX-II computers. In addition to several locally written programs, the following software was used: TRACER by S. L. Lawton and R. A. Jacobson; G. M. Sheldrick's SHELX76 and SHELX84; FMLS, a highly modified version of W. R. Busing and H. A. Levy's ORFLS; XANADU from P. Roberts and G. M. Sheldrick; R. E. Davis' DAESD; and C. Johnson's ORTEP.

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(10) ^{13}C NMR (75 MHz, cyclohexane-d_{12}) δ 3.0 (q, J = 120 Hz, $SiMe_3$), 36.4 (d, J = 131 Hz, C-1), 128.6 (d), 129.2 (d) and 153.2 (s) (C_6H_5); ^{13}C NMR (75 MHz, THF-d_8) δ 3.09 (q, J = 117.2 Hz, $SiMe_3$), 3.17 (q, J = 117.4 Hz, $SiMe_3$), 40.63 (d, J = 141.7 Hz, C-1), 126.11 (d), 127.6 (d), 127.7 (d), 159.6 (s) (C_6H_5); ^1H NMR (300 MHz, THF-d_8) δ 0.00 (s, $SiMe_3$, 9 H), 0.10 (s, $SiMe_3$, 9 H), 1.05 (s, 1–H, 1 H), 7.06–7.23 (m, 3 H), 7.89–7.92 (m, 2 H) (C_6H_5).

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