phosphorus–rhodium coupling at high temperatures indicates that the exchange process is intramolecular, and from an estimated exchange rate of 500 sec^{-1} at $-107°$ we obtain a free energy of activation, $\Delta G^{\ddagger}$, of 7.4 kcal mol^{-1}. The barrier is higher than anticipated and, as a result, the spectra show some evidence for inequivalence of the ligands at temperatures as high as ~ -50 to $\sim -70°$ (Figure 2). The possibility should not be overlooked that interactions with the counterion may contribute to the barrier, although any interaction of this type must be averaged rapidly on the nmr time scale even at very low temperatures. As noted above, however, for transition metal hydrides of the form HML_4 and HML_4^-, barriers for isoelectronic pairs are similar,[8] suggesting that the contribution from ion pairing is small. (The barriers are, in fact, smaller for the ionic species.)

For a D_{3h} ML_5 system, there are two possible types of temperature-dependent nmr line shapes[8] (three basic permutational sets[11] including the identity). One of these (which includes the Berry[12] process) involves the simultaneous exchange of the axial ligands with two of the equatorial ligands. The other involves single axial–equatorial exchanges. We are currently undertaking a complete density matrix line shape analysis[11] of these spectra in order to distinguish between these two possibilities.

(11) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

(12) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

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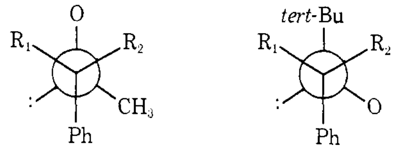
Kinetic Preference between the Diastereotopic Hydrogens in the Lithiation of Benzyl Methyl and Benzyl *tert*-Butyl Sulfoxides

Sir:

In previous communications[1] we have described the thermodynamic preference of one of the two diastereotopic lithio derivatives of benzyl methyl and benzyl *tert*-butyl sulfoxides by trapping the lithio derivatives (α-sulfinyl carbanions) with an excess of several reactive electrophiles (D_2O, acetone, CH_3I). In the case of benzyl methyl sulfoxide the isomer, **1**, having the *S*,*S*[2] configuration was preferred over the *R*,*S* isomer, **2**, by approximately 15:1 in THF at $-60°$, while for benzyl *tert*-butyl sulfoxide the preference of the *S*,*S* isomer **3** was so large that the presence of **4**, the *R*,*S* isomer, could not be detected by nmr analysis of the crude trapping products.[1b]

In view of the considerable work on the kinetic preference observed in the exchange of the diastereotopic hydrogens α to sulfoxides,[1,3] we would like to present our results on the relationship between the kinetic and thermodynamic preferences. In addition, Nishihata and Nishio[4] have reported isotope effects and selectivity factors in the lithiation of benzyl methyl[4a] and benzyl *tert*-butyl sulfoxides[4b] which differ significantly from ours.



1 (*S*,*S*), $R_1 = Li$; $R_2 = H$
2 (*R*,*S*), $R_1 = H$; $R_2 = Li$
5 (*S*,*S*), $R_1 = D$; $R_2 = H$
6 (*R*,*S*), $R_1 = H$; $R_2 = D$
3 (*S*,*S*), $R_1 = Li$; $R_2 = H$
4 (*R*,*S*), $R_1 = H$; $R_2 = Li$
9 (*S*,*S*), $R_1 = D$; $R_2 = H$

The kinetic preference for the removal of the diastereotopic hydrogens in benzyl methyl sulfoxide was determined using the method described by Eliel, *et al.*[5] Several samples of α-deuteriobenzyl methyl sulfoxide of known configuration[1] and isotope content were each treated with methyllithium at $-60°$ for 1 min and then quenched with excess CH_3I (eq 1). The α-methylbenzyl methyl sulfoxides, **7** and **8**, thus obtained were examined for deuterium content by nmr[6] (see Table I).

$$\mathbf{5} + \mathbf{6} \xrightarrow{CH_3Li} \mathbf{1} + \mathbf{2} \xrightarrow{CH_3I} \underset{\mathbf{7}}{PhCH(CH_3)S(O)CH_3} + \underset{\mathbf{8}}{PhCD(CH_3)S(O)CH_3} \quad (1)$$

Table I. Reaction of $PhCHDS(O)CH_3$ with CH_3Li followed by CH_3I

Starting materials[a]		Products[6]	
% **5**	% **6**	% **7**	% **8**
92	8	39	61
53	47	30	70
6	94	20	80

[a] Ratios were measured in DMSO-d_6 solution using a Varian HA-100 spectrometer equipped with deuterium decoupling; error ±5%.

Appropriate corrections for the presence of nondeuterated and dideuterated sulfoxides, as determined from mass spectra, were made.

The isotope effect[7] (IE $= k_H/k_D$) and the selectivity factor ($S = k_{H_S}/k_{H_R}$) were calculated using the equations[8] $\mathbf{7}/\mathbf{8} = N_5(S/IE) + N_6/S \times IE$ and $\mathbf{8}/\mathbf{7} = N_5(IE/S) + N_6(S \times IE)$; N_5 and N_6 = mole fractions of **5** and **6**, respectively.

The solution of these equations gives an isotope effect of 2.5 ± 0.4 and a selectivity factor 1.7 ± 0.3.[9]

The magnitude of the isotope effect is reasonable for

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(1) (a) T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, *Can. J. Chem.*, **48**, 2148 (1970); (b) T. Durst, R. Viau, and M. R. McClory, *J. Amer. Chem. Soc.*, **93**, 3077 (1971).

(2) Although we were working with racemic mixtures, all formulas are presented and discussed in terms of the sulfur chirality as *S*.

(3) (a) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Amer. Chem. Soc.*, **94**, 8795 (1972), and references therein; (b) A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *ibid.*, **87**, 5498 (1965); (c) J. E. Baldwin, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 1415 (1969); (d) M. Bullock, J. W. M. Scott, and P. D. Golding, *ibid.*, 168 (1967); (e) M. Nishio, *ibid.*, 562 (1968).

(4) (a) K. Nishihata and M. Nishio, *J. Chem. Soc., Perkin Trans. 2*, in press; (b) M. Nishio, *Tetrahedron Lett.*, 4839 (1972).

(5) E. L. Eliel, A. A. Abatjoglou, and A. A. Hartmann, *J. Amer. Chem. Soc.*, **94**, 4786 (1972).

(6) Carried out on a Varian HA-100 spectrometer by comparison of the integrals due to $CHCH_3$ (d) and $CDCH_3$ (s) during deuterium decoupling.

(7) It is assumed that the isotope effects for the *pro-S* and *pro-R* hydrogens are approximately equal, *cf.* Eliel, *et al.*[5]

(8) D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, **75**, 6011 (1953).

(9) These values contrast with those obtained by Nishihata and Nishio[4a] who reported IE = 7 and *S* = 0.66 for the reaction of **5** and **6** with *n*-BuLi in THF at $-70°$. A selectivity factor <1 is highly unlikely since it implies that the less stable carbanion **2** is formed more readily than the more stable carbanion **1**.

the reaction in question[10,11] and is approximately the same as that found by Eliel, *et al.*,[5] for the reaction of 1,3-dithianes with n-BuLi ($k_H/k_D = 2.5 \pm 0.1$).

When a similar reaction was carried out on S,S α-deuteriobenzyl *tert*-butyl sulfoxide (**9**), greater than 99% diastereomerically pure (nmr) and free of d_2 (mass spectrometry), the methylated product **10** contained 2.1 ± 0.2% deuterium.[12] Assuming that the isotope effect for **9** is the same as for benzyl methyl sulfoxide, the kinetic selectivity for the removal of the *pro-S vs.* the *pro-R* hydrogen is calculated to be $(97.9/2.1)(2.5 \pm 0.4) = 117 \pm 20$. At $-60°$ this represents a free energy difference of 2.17 kcal/mol between the two transition states.

A kinetic selectivity of >100:1 for the exchange of diastereotopic hydrogens α to a sulfoxide function is not exceptional in conformationally fixed systems where selectivities greater than 1000:1 have been reported.[13] The novelty of the high selectivity observed in **9** is that it occurred in an open-chain system and more importantly with a base whose pK_a is about 13 pK_a units greater than that of the α hydrogens of **9**.[14]

The high selectivity in **9** can be most readily explained by assuming that benzyl *tert*-butyl sulfoxide exists almost exclusively in the trans conformation (as depicted) in which the removal of the *pro-S* hydrogen is strongly favored over the removal of the *pro-R* hydrogen by a stereoelectronic factor.[15]

An estimate of the energy difference between lithio derivatives **3** and **4** can be obtained from the following line of reasoning. The kinetic preference factor of 1.7:1 at $-60°$ for the *pro-S* hydrogen in benzyl methyl sulfoxide is equal to a difference in transition state energies for the removal of the *pro-S vs. pro-R* hydrogen of 0.23 kcal/mol. The thermodynamic preference of 15:1 at $-60°$ for the S,S lithio derivative **1** *vs.* the R,S derivative **2** is equal to a 1.15-kcal/mol free energy difference. If the removal of the *pro-S* and *pro-R* hydrogens in benzyl methyl sulfoxide leads initially to the lithio derivatives **1** and **2**, then the relationship between the transition state energy differences for their formation and their ground state energy differences (Brønsted coefficient α) is $0.23/1.15 = 0.20$.[16]

Finally, if the relationship between transition state and ground state energy differences is similar for the two sulfoxides, then the energy differences between **3** and **4** can be estimated as $2.17/0.20 = 10.8$ kcal, in accordance with expectations based on the calculations.[15] The solvent, which was neglected in the calculations, has been shown to play a predominant role in the stability of carbanions in different conformations with respect to the sulfur asymmetry.[1a,3a,17] The correspondence between the calculations and the experimental results is poor in the highly polar solvents[3a,17] but would be expected to be considerably better in the relatively nonpolar THF which more closely approximates the gas-phase calculations.

Finally, the results obtained in the *tert*-butyl benzyl system clearly show that the deprotonation with CH_3Li and the protonation (deuteration) of the α-lithiobenzyl derivative[1b] occur *via* the same stereochemical course, the more likely one being retention of configuration in each step.[18]

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[10] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 167–168.

[11] An isotope effect of 2.3 ± 0.2 was found for the reaction of $PhCHDSO_2$-*tert*-Bu with CH_3Li in THF at $-60°$: R. Viau, unpublished observations.

[12] The D content was determined by comparison of the heights of the $C_7{}^{13}CH_9$ and C_8H_8D peaks obtained at 12 eV using an A.E.I.M.S.9 mass spectrometer equipped with signal averager.

[13] R. R. Fraser and F. J. Schuber, *Chem. Commun.*, 397 (1969).

[14] The pK_a of methane is ~40. F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, **89**, 3905 (1967), have shown that the change $CH_3SO_2CH_3$ to $PhCH_2SO_2CH_3$ lowers the pK_a from 28.5 to 22. A similar decrease in going from DMSO (pK_a = 33.5) to $PhCH_2S(O)CH_3$ gives the latter a pK_a of about 27.

[15] *Ab initio* calculations by A. Rauk, S. Wolfe, and I. G. Csizmadia, *Can. J. Chem.*, **47**, 113 (1969), indicated that a carbanion trans to oxygen, *e.g.*, **3**, was considerably more stable than one trans to the sulfur lone pair, *e.g.*, **4**.

[16] An α value of <0.5 is expected for an exothermic reaction: ref 10, pp 156–161.

[17] J. B. Hutchinson, K. K. Andersen, and A. R. Katritzky, *J. Amer. Chem. Soc.*, **91**, 3839 (1969).

[18] The financial assistance of the National Research Council of Canada is gratefully acknowledged.

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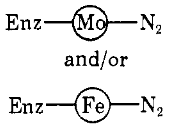
Nonenzymic Nitrogen Fixation by an Iron–Molybdenum Model for Nitrogenase

Sir:

Current interpretation[1] of enzymic nitrogen (N_2) fixation features the cooperative action of the two metals present in nitrogenase, molybdenum and iron, believed to be instrumental in N_2 coordination (**1**) and reduction, carried to the NH_3 level by means of a ferredoxin-like moiety (**2**).[2,3] We report now a nitrogenase model reaction in which significant amounts of NH_3 are produced when the Mo–N_2 coordination compound **3**[4] is added to the diphenyldithiolene Fe–S cluster **4**,[3,5] reduced to the 4−, or lower, level. Experiments described herein are, to our knowledge, the first to involve (a) NH_3 synthesis by direct reduction of relatively stable transition metal–N_2 complexes,[6,7] and



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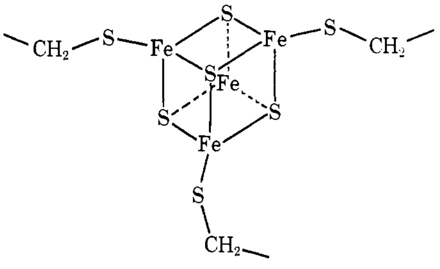

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[1] R. W. F. Hardy, R. C. Burns, and G. W. Parshall, *Advan. Chem. Ser.*, No. 100, 219 (1971), and references cited therein.

[2] Structure of ferredoxin: L. C. Sieker, E. Adman, and L. H. Jensen, *Nature (London)*, **235**, 40 (1972); C. W. Carter, J. Kraut, S. T. Freer, P. A. Alden, L. C. Sieker, E. Adman, and L. H. Jensen, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3526 (1972).

[3] For clarity, the ligand on the rear iron atom has been omitted from structures 2 and 4.

[4] J. Chatt and A. G. Wedd, *J. Organometal. Chem.*, **27**, C15 (1971); (b) T. A. George and C. D. Seibold, *ibid.*, **30**, C13 (1971); (c) M. Hidai, K. Tominari, and Y. Uchida, *J. Amer. Chem. Soc.*, **94**, 110 (1972).

[5] (a) Preparation: G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *ibid.*, **88**, 4609 (1966); (b) structure: A. L. Balch, *ibid.*, **91**, 6962 (1969). An X-ray determination on the structurally analogous bis(trifluoromethyl) dithiolene in the 2− oxidation state was recently published by I. Bernal, B. R. Davis, M. L. Good, and S. Chandra, *J. Coord. Chem.*, **2**, 61 (1972).

[6] For NH_3 formation from an isolable, but unstable, N_2 coordination compound of titanocene, see: (a) E. E. van Tamelen, R. B.