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 ± 0.4) = 117 ± 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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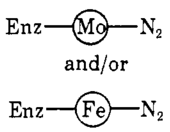
Nonenzymic Nitrogen Fixation by an Iron–Molybdenum Model for Nitrogenase

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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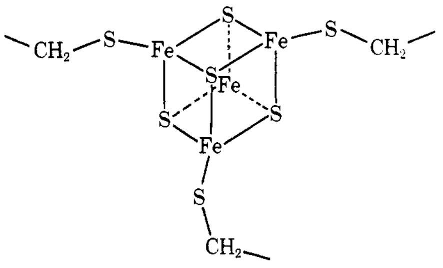

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[1] R. W. F. Hardy, R. C. Burns, and G. W. Parshall, *Advan. Chem. Ser.*, No. **100**, 219 (1971), and references cited therein.

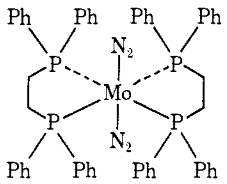
[2] Structure of ferredoxin: L. C. Sieker, E. Adman, and L. H. Jensen, *Nature* (*London*), **235**, 40 (1972); C. W. Carter, J. Kraut, S. T. Freer, P. A. Alden, L. C. Sieker, E. Adman, and L. H. Jensen, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3526 (1972).

[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.



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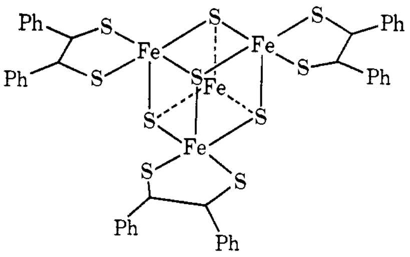

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(b) N_2 fixation by agents of the ferredoxin structural type.

After the slow addition of a THF solution of **3**[8] (0.4 mmol in 100 ml) to a solution containing 2 equiv of **4** and 8 equiv of sodium naphthalenide (NaNp), all at room temperature, the reaction mixture was allowed to stir for 20 hr. Visible and infrared spectroscopy indicated that the NaNp was completely consumed prior to the addition of **3**.[9] After the addition of 20% aqueous HCl,[11] solvent was removed and the NH_4Cl was extracted from the residue with H_2O. Nessler tests were positive, and the NH_3 yields as determined by the Kjeldahl method[12] ranged from 0.013 to 0.044 mmol/mmol of **3**.[13] Ammonia yields were also measured using an NH_3 gas electrode,[14] and fell at levels at least 85% of those determined by the Kjeldahl method. When a reduction of **3** was carried out as above, but in the presence of 16 equiv of NaNp, the yield rose to as high as 0.268 mmol of NH_3/mmol of **3**.

Additional novel N_2 fixations were uncovered which bear on the reaction pathway involving **3** and **4**. The Mo complex **3** itself, although produced in the presence of metallic Mg or Na·Hg,[4a,b] is reducible by excess NaNp to ammonia (0.100–0.300 mmol of NH_3/mmol of **3**) as are $[Mo(N_2)_2(dppe)_2]^+I_3^-$[15] (0.040–0.085) $ReClN_2(dppe)_2$[16] (0.017–0.025), and $IrClN_2(PPh_3)_2$[17] (0.065–0.100), substances of the type previously considered refractory toward reducing agents with a potential up to and including that of metallic Na.[18] No N_2H_4 formation was observed in any of these reductions, and NaNp *per se* does not of course fix N_2. Further, the iron–dithiolene system **4** alone is capable of fixing molecular N_2. At the 4− level, this inorganic agent, under a N_2 atmosphere or in the presence of 2 equiv of N_2 rapidly circulated through the solution under argon, led to formation of up to 0.137 mmol of NH_3/mmol of $\mathbf{4}^{4-}$. When a *ca.* 300 molar excess of NaNp was added to **4** under N_2, yields rose to 0.259–0.269 mmol of NH_3/mmol of **4**. Similar fixation results were secured with the Fe–S cluster $(FeSC_5H_5)_4$.[19]

In consideration of the yield data herein, preliminary rate data on N_2 dissociation from $Mo(N_2)_2(dppe)_2$ in THF, and the evidence that **3** undergoes ready conversion with CO to $Mo(CO)_2(dppe)_2$ by means of first-order loss of N_2 followed by CO combination,[4c] we believe it likely that NH_3 formation from **3** and $\mathbf{4}^{n-}$ involves predominant initial release of N_2 from **3**, followed by coordination and reduction by $\mathbf{4}^{n-}$. At the present time little evidence as to the detailed *chemical* mechanism of biological N_2 coordination–reduction is available, and overall enzymic fixation by initial N_2 coordination followed by transfer of N_2 to the reduction site remains a distinct possibility.

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Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969); (b) J. E. Bercaw and H. H. Brintzinger, *ibid.*, **93**, 2045 (1971); (c) R. H. Marvich and H. H. Brintzinger, *ibid.*, **93**, 2046 (1971); (d) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *ibid.*, **94**, 1218 (1972); (e) E. E. van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, 481 (1972).

(7) (a) For the HCl-promoted conversion of 3 to $MoCl_2(N_2H_2(dppe)_2$, see J. Chatt, G. A. Heath, and R. L. Richards, *ibid.*, 1010 (1972); (b) in the case of NH_3 formation by reaction of $(PPh_3)_3CoH(N_2)$, naphthalene, Li, and $TiCl_4$ (or $MoCl_5$, $CoCl_2$, $FeCl_3$), reported by M. E. Vol'pin, V. S. Lenenko, and V. B. Shur, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 463 (1971), transfer of the N_2 ligand from Co to Ti, followed by reduction of Ti-bound N_2,[6] was not ruled out.

(8) Water and oxygen were removed from THF by distillation under argon from sodium benzophenone ketyl. All experiments were conducted under argon, unless noted, using standard vacuum line techniques.

(9) From polarographic data[5,10] it can be inferred that 4 will react with 4 equiv of NaNp to produce 4^{4-}.

(10) S. Wawzonek and H. A. Laitinen, *J. Amer. Chem. Soc.*, **64**, 2365 (1942).

(11) Purified by distillation. All other aqueous reagents utilized in the work-up were prepared from doubly distilled degassed water.

(12) Titrations were followed potentiometrically and yields were graphically determined from *ca.* 20 data points. Each was corrected for a small blank.

(13) All experiments were conducted at least in triplicate and the full range of yields is reported.

(14) An Orion Model 95-10 ammonia gas electrode was utilized, and the yields were determined by known additions of standard NH_4Cl solutions, the original concentrations being extrapolated using 100% volume corrected Gran's Plot Paper.

(15) T. A. George and C. D. Seibold, *J. Amer. Chem. Soc.*, **94**, 6859 (1972); dppe = 1,2-bisdiphenylphosphinoethane.

(16) J. Chatt, J. R. Dilworth, and G. J. Leigh, *Chem. Commun.*, 687 (1969).

(17) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **88**, 3459 (1966).

(18) These dinitrogen complexes are stable as solids in air for days, except for $IrClN_2(PPh_3)_2$, which survives only several hours without noticeable decomposition.

(19) Synthesis: R. A. Schunn, C. J. Fritchie, and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966). Structure: C. H. Wei, G. R. Willas, P. M. Treichel, and L. F. Dahl, *ibid.*, **5**, 900 (1966).

(20) National Science Foundation Fellow, 1971–present.

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Mechanism of Ozonolysis. Conformations of Propylene and *trans*-2-Butene Ozonides[1]

Sir:

In a previous report[2] it was shown that ethylene ozonide has the O–O half-chair conformation with C_2 symmetry. We have now determined that propylene and *trans*-2-butene ozonides have the same half-chair conformation as ethylene ozonide. This observed conformation is different from that postulated by the Bauld–Bailey syn–anti zwitterion mechanism for final ozonides with bulky substituents.[3] We have also found that the cis/trans ratio for 2-butene ozonide obtained as a cross ozonide from propylene differs significantly from that obtained as a normal ozonide from *cis*- or *trans*-2-butene. The syn–anti zwitterion mechanism is

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(1) Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work.

(2) C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **94**, 6336 (1972).

(3) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).