enhance the appositeness of $MoFe_3S_4$ clusters as synthetic representations of the nitrogenase Mo site at this early stage of development in the modeling problem.

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(22) McDonald, J. W.; Friesen, G. D.; Newton, W. E. *Inorg. Chim. Acta* **1980**, *46*, L79.

Isotope Scrambling with ^{15}N-Labeled Azide Ion and *p*-Toluenesulfonyl Azide[1a]

Carla Casewit,[1b] J. Wenninger,[1c] and John D. Roberts*

Contribution No. 6403
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

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p-Toluenesulfonyl azide (**1**) reacts with azide ion in dimethyl sulfoxide solution to form *p*-toluenesulfinate anion and dinitrogen (eq 1, Ts = $4\text{-}CH_3C_6H_4SO_2^-$).[2] For a determination of whether

$$\underset{\mathbf{1}}{TsN_3} + N_3^- \rightarrow Ts^- + 3N_2 \qquad (1)$$

or not there are solvent effects on this reaction, it has been studied in other solvents by ^{15}N NMR spectroscopy using potassium azide-*1,3*-$^{15}N_1$ (99%) as a tracer. In dichloromethane using potassium azide solubilized with 18-crown-6,[3] azide-ion exchange (eq 2) leading to **1**-*1,3*-$^{15}N_1$ takes place, just as it does in dimethyl

$$TsN_3 + {}^{15}N{=}N{=}N^- \rightarrow Ts{-}{}^{15}N{=}N{=}N + Ts{-}N{=}N{=}{}^{15}N + N_3^- \qquad (2)$$

sulfoxide. However, in this solvent, reaction 1 does not occur. Instead, ^{15}N NMR spectra[4a] (Figure 1), show a slow and unexpected formation of **1**-*2*-^{15}N (eq 3). The metathesis products of

$$TsN_3 + {}^{15}N{=}N{=}N^- \rightarrow Ts{-}N{=}{}^{15}N{=}N + N_3^- \qquad (3)$$

1 with azide-*1,3*-$^{15}N_1$, **1**-*1*-$^{15}N_1$ (236.5 ppm), and **1**-*3*-^{15}N (133.3 ppm) form quickly in accord with eq 2 (Figure 1a). The resonance of the terminal nitrogen of azide ion is strong at 275.8 ppm. The signals at 154.0 and 295.6 ppm result from an as yet unidentified product of a separately observable reaction of azide ion with dichloromethane. After 5 days (Figure 1b), no azide ion remained, and there is clear formation on the order of 10% of **1**-*2*-^{15}N (142.5 ppm).[4b]

The formation of *p*-toluenesulfonyl azide-*2*-^{15}N is consistent with addition of labeled azide ion to **1** to give a *p*-toluenesulfonylhexazene (**2**) (eq 4) which could give ^{15}N scrambling of

$$Ts{-}N{=}N{=}N + {}^{15}N{=}N{=}N^- \rightarrow Ts{-}N^-{-}N{=}\underset{\mathbf{2}}{N}{-}{}^{15}N{=}N{=}N \qquad (4)$$

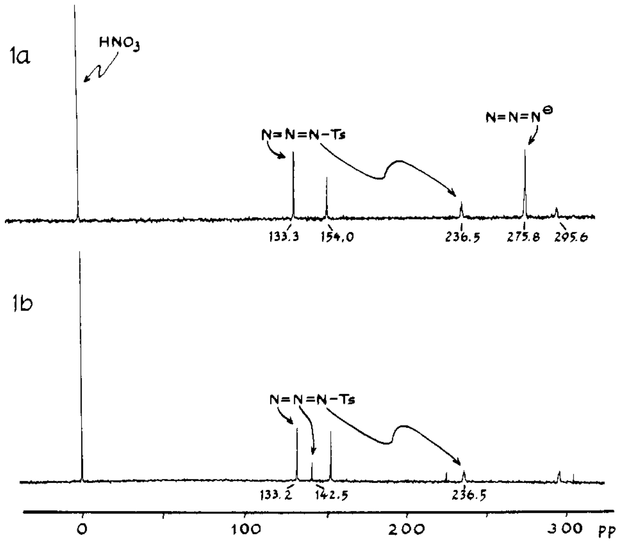
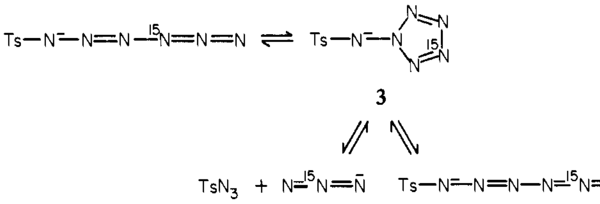


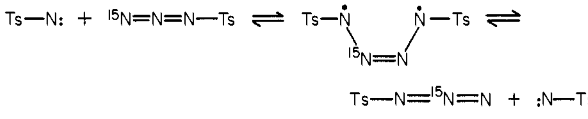
Figure 1. ^{15}N spectra of a solution containing 5.9×10^{-3} mol of potassium azide-*1,3*-$^{15}N_1$, 6.1×10^{-3} mol of **1**, and 6.7×10^{-3} mol of 18-crown-6 in 30 mL of dichloromethane, taken with a 20-μs pulse and 10-s repetition rate in a Bruker WH-180 spectrometer[4a] at 25 °C. (a) Spectrum started immediately after preparation, 3748 transients; (b) five days after preparation, 5213 transients. The signals at 225 ppm and 304 ppm are artifacts of the instrument.

the *azide ion* if it were to be involved in *reversible* formation of the *N*-pentazole derivative **3** (eq 5).[5,6] Once azide-*2*-^{15}N is formed,



(5)

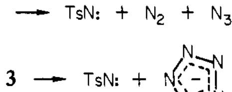
then metathesis between **1** and this ion would lead to **1**-*2*-^{15}N. The only reasonable alternative we have so far devised to formation of **3** for the observed ^{15}N scrambling is a chain addition–dissociation of singlet[7] *p*-toluenesulfonylnitrene and **1**-*3*-^{15}N (eq 6).[8]



(6)

$$\mathbf{2} \longrightarrow TsN{:} + N_2 + N_3^- \qquad (7)$$

$\mathbf{3} \longrightarrow TsN{:} +$



(8)

Possible *p*-toluenesulfonylnitrene precursors include **2** and **3**. Loss of dinitrogen and azide ion from **2**[9] (eq 7) or elimination of pentazole anion from **3**[10] (eq 8) would be expected to give the

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(1) (a) Supported by the National Science Foundation. (b) IBM Graduate Fellow, 1979–1980. (c) DAAD Postdoctoral Fellow, 1980–1981.

(2) Casewit, C.; Roberts, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 2364–2368.

(3) Gokel, G. W.; Durst, H. D. *Aldrichim. Acta* **1976**, *9*, 3–12.

(4) (a) The ^{15}N spectra were measured at 18.25 MHz with a Bruker WH-180 spectrometer using 25-mm sample tubes. Lock and reference signals were provided by a concentric 5-mm tube containing 1 M 95% $H^{15}NO_3$ in D_2O solution. Spectra were proton coupled and obtained at ambient probe temperature. (b) A mixture of 1-, 2-, and 3-^{15}N-labeled **1**[2] in dichloromethane shows ^{15}N resonances at 133.2 (N3), 142.4 (N2), and 236.5 (N1) ppm. Shift assignments are based on ^{15}N labeling experiments reported by: Duthaler, R. O.; Förster, H. G.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4974–4979. The N1 resonance for potassium azide-*1*-^{15}N in dichloromethane, solubilized by 18-crown-6, comes at 275.8 ppm.

(5) The reaction of heterocyclic azidinium salts with azide ion is also thought to involve substituted hexazene intermediates. Balli, H. *Helv. Chim. Acta* **1974**, *57*, 1912–1919.

(6) A similar ring-chain equilibrium has been postulated for the reaction of aryldiazonium salts with azide ion. Smith, P. J.; Westaway, K. C. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Interscience: New York, 1978; pp 716–717.

(7) Nitrene singlet-to-triplet intersystem crossing is inhibited by dichloromethane. Casagrande, P.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* **1978**, *43*, 2725–2726.

(8) It should be noted that attack of electrophilic *p*-toluenesulfonylnitrene on the terminal nitrogen of **1** would be not an expected reaction because the terminal nitrogen of **1** normally reacts with nucleophiles. Breslow, D. S. In "Nitrenes"; Lwowski, Ed.; Interscience: New York, 1970; Chapter 8.

(9) See ref 2 for a similar decomposition in the coupling of azide ion with heterocyclic azidinium salts.

(10) Some related compounds have been investigated as possible sources of *p*-toluenesulfonylnitrene by: Abramovitch, R. A.; Takaya, T. *J. Org. Chem.* **1973**, *38*, 3311–3316. Abramovitch, R. A.; Bailey, T. D.; Takaya, T.; Uma, V. *J. Org. Chem.* **1974**, *39*, 340–345.

nitrene intermediate. However, irradiation of **1**-*1,3*-$^{15}N_1$ in dichloromethane in the presence of 18-crown-6 under conditions in which dinitrogen is formed, presumably by way of the nitrene, gave no evidence for formation of **1**-*2*-^{15}N. Similar results were obtained by irradiation of **1**-*3*-^{15}N in toluene where formation of the nitrene was indicated by *p*-toluenesulfonylamido insertion products resulting from attack of the nitrene on the solvent.

Interestingly, addition of 1 equiv of potassium iodide to a solution of **1**, potassium azide-*1*-^{15}N, and 18-crown-6 in dichloromethane inhibits formation of **1**-*2*-^{15}N. The iodide ion appears to intercept **2** causing decomposition to *p*-toluenesulfinate ion, azide ion, and iodoazide (eq 9), before cyclization or other

$$\mathbf{2} + I^- \rightarrow Ts^- + N_3^- + IN_3 \qquad (9)$$

reactions occur. Dinitrogen and iodine, products of the reaction of iodoazide[11] with iodide and azide ion, are in fact observed.[12]

The reaction of **1** with azide ion is strongly solvent dependent. In dimethyl sulfoxide, although **2** is probably formed,[2] decomposition to dinitrogen and *p*-toluenesulfinate is rapid. In dichloromethane, the major reaction in dimethyl sulfoxide is depressed, and eq 3 is dominant. In toluene with 18-crown-6 present, the reactions of eq 1 and 3 occur simultaneously. The origin of solvent effects is not clear, and research on the mechanism of these nitrogen scrambling reactions is under way.

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[11] Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 507–514.

[12] Similar decomposition reactions have been reported for bromoazide. Griffith, R. O.; Irving, R. *Trans. Faraday Soc.* **1949**, *45*, 563–575.

Semibullvalenes. 1. Synthesis and Crystal Structure of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)tricyclo-[3.3.0.0^{2,8}]octa-3,6-diene—A Donor-Acceptor-Substituted Semibullvalene

L. S. Miller, K. Grohmann,* and J. J. Dannenberg

Department of Chemistry, Hunter College
City University of New York
New York, New York 10021

L. Todaro

Research Division, Hoffmann-La Roche Inc.
Nutley, New Jersey 07110

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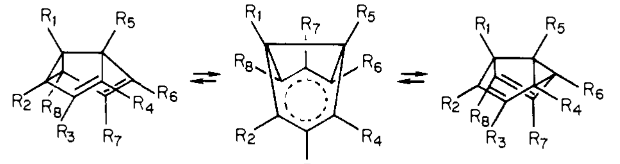
Semibullvalenes undergo a facile Cope rearrangement (I ⇄ I′) whose energy barrier is the lowest known to date[1,2] (eq 1). This barrier has been calculated[1] to be 3.6 kcal/mol and found experimentally[2] to be 5.5 kcal/mol for the unsubstituted compound (Ia). Both extended Hückel[3] and MINDO-2[1] calculations have been used to assess the effects of ring substituents on the energy barrier for this rearrangement. On these bases, π-electron donors on positions 1 and 5 and π-electron acceptors on positions 2, 4, 6, and 8 of I are expected to lower the activation energy for Cope rearrangement and, perhaps, to yield a species with a stabilized transition state, i.e., a "bishomobenzene"-type structure (II).



Ia, R_1-R_8 = H
b, $R_1 = R_5 = CH_3$; $R_2 = R_4 = R_6 = R_8 = COOCH_3$; $R_3 = R_7 = H$

II

I′

(1)

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[1] Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 7201.

[2] Cheng, A. K.; Anet, F. A.; Mioduski, J.; Meinwald, J. *J. J. Am. Chem. Soc.* **1974**, *96*, 2887.

[3] Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941.

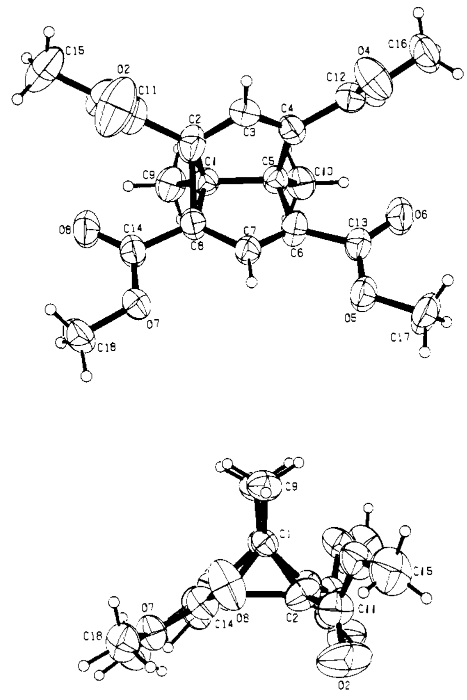

Figure 1. Structure of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)-semibullvalene (Ib), showing the 50% thermal ellipsoids. Hydrogen atoms are not labeled.

We wish to report the synthesis and X-ray structure determination of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (Ib). The new synthetic route is outlined in Scheme I.[4] Enol **1**[5] was converted into the tetracyclic ketone **3**[6] by successive bromination and cyclizing dehydrobromination. Diketone **3** was stereospecifically reduced to *exo*-diol **4**[6] by using $(i\text{-}Bu)_3Al$.[7] The corresponding dimesyl derivative **5**[6] was refluxed with an excess of sodium iodide in acetone in order to form Ib through a conjugate 1,4-elimination reaction.[8] After 1 h a white solid could be isolated whose spectra were consistent with the monoiodomonomesyl compound **6**.[9] After several hours of reflux a new yellow compound (Ib)[6] was isolated. Longer reflux produced a side product whose structure is currently being elucidated.[10] Crystals of Ib suitable for X-ray crystallography were obtained by recrystallization from CH_3OH.

Compound Ib is a bright yellow crystalline solid which melts at 102.5–103 °C. Spectral characteristics[11] are as follows: IR ($CHCl_3$) 3010, 2950, 1725, 1595, 1435, 1335, 1200–1250, 1055, 1040 cm^{-1}; UV λ_{max} (EtOH) 232 nm (ε 12 400); ^{1}H NMR[11] 1.45 (s, 6 H, CH_3), 3.67 (s, 12 H, OCH_3), 6.18 (br s, 2 H, H3,7); ^{13}C NMR[11] 11.02 (C9,10), 52.09 (OCH_3), 68.67 (C1,5), 104.07 (C2,4,6,8), 131.23 (C3,7), 165.47 (C=O).

The ^{1}H and ^{13}C NMR spectra both clearly show averaged signals for carbons 1 and 5, carbons 2, 4, 6, and 8, and for the proton-bearing groups attached to these carbons. The 270-MHz

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[4] Complete experimental details will be published in a subsequent paper.

[5] (a) Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885. (b) ^{1}H and ^{13}C NMR spectra are consistent with the totally enolized structure. See also: Camps, P. *Tetrahedron Lett.* **1974**, 4067.

[6] All new compounds gave satisfactory spectroscopic and elemental analyses.

[7] (a) Roberts, M.; Parsons, W.; Schlessinger, R. J. *J. Org. Chem.* **1978**, *43*, 3970. (b) Other reducing agents gave different stereoisomers or mixtures.

[8] See (a) Birladeanu, L.; Harris, D. L.; Winstein, S. J. *J. Am. Chem. Soc.* **1970**, *92*, 6387. (b) Birladeanu, L.; Chamot, E.; Fristad, W.; Paquette, L.; Winstein, S. *J. Org. Chem.* **1977**, *42*, 3260.

[9] Compounds 6: ^{1}H NMR ($CDCl_3$) 1.53 (s, 6 H), 2.91 (s, 3 H), 3.63, 3.65 (2s, 12 H), 5.38 (s, 1 H), 6.06 (s, 1 H) ppm. Upon reheating with sodium iodide in acetone, **6** reacted further to form **Ib**.

[10] **Ib** isomerizes to this compound upon heating or prolonged standing in solution.

[11] ^{1}H NMR spectra were measured in $CDCl_3$ on a Varian A-60 spectrometer, ^{13}C NMR were measured in $CDCl_3$ on a JEOL-PFT100 instrument. All signals are reported in ppm downfield from Me_4Si. IR spectra were recorded in $CHCl_3$.