to 1.3 V in another cell produced the results shown in Figure 2. Under these conditions reoxidation is quantitative, and the three peaks have the same potential separation for both negative and positive sweeps.

It is interesting to note that the roughly constant 0.5-V separation between waves A and B, B and C, and C and D corresponds approximately to the electron-by-electron reduction in solution (up to C_{60}^{4-}).[3] This could be interpreted as evidence for weakly perturbed molecular orbitals in the solid state which continue to dominate the electroactivity. On the other hand, the succession of waves leading to $x = 3$ could be assigned to full occupancy of octahedral (O) and tetrahedral (T) sites in the fcc lattice, as in the superconducting compounds with K and Rb.[16] Similarly, $x = 4$ could be assigned to the recently-discovered body-centered tetragonal phase,[17] which can be viewed as a shear-distorted fcc structure with the correct symmetry to eventually transform to the (saturated) body-centered cubic phase at $x = 16$.[18] This latter interpretation would provide a natural explanation for the lack of reversibility upon reducing to $x = 4$ which exceeds the fcc isostructural range. However, preliminary X-ray studies on positive composite electrode materials reduced at 2.2 and 1.3 V (i.e., $x = 0.5$ and $x = 3$, respectively) give new diffraction patterns which do not correspond to those of the K and Rb compound structures.[6,16] In situ X-ray diffraction experiments, with all-solid-state electrochemical cells built in the same way as the coin ones used in this study, are currently in progress. The phase diagram of this system turns out to be far more complex than originally envisioned.

Acknowledgment. Research at Penn was supported by the National Science Foundation through the Materials Research Laboratory Program, Grant No. DMR-88-19885, and by Grant No. DMR-89-01219.

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Estimation of Dynamic Effects on Product Ratios by Vectorial Decomposition of a Reaction Coordinate. Application to Thermal Nitrogen Loss from Bicyclic Azo Compounds

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Application of the traditional models of kinetics to the calculation of product ratios in thermal reactions is possible only when there are potential energy barriers to the competing processes. In reactions where branching to products occurs *after* the rate-determining transition state, the traditional models can therefore not be applied.[1] In this communication we propose a model for estimating the product ratios in such reactions by approximating the reaction dynamics, without resort to trajectory calculations. The model is illustrated for thermal reactions of bicyclic azo compounds but could have application to other systems.

The thermal extrusion of nitrogen from 2,3-diazabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-d_2 (**1**, see Figure 1) is believed[2] to occur via the diazenyl biradical **2** and has been known for some time[3] to yield the inverted structure bicyclo[2.1.0]pentane-*exo,exo*-2,3-d_2 (**4x**) as the major product. We have recently[4] interpreted this result with the help of classical trajectory calculations on a model three-dimensional projection of the potential energy surface for conversion of **2** to **3**, **4x**, and **4n**. The alternative analysis presented here is complementary to the previous work in the sense that it treats the problem in its full dimensionality but does not involve calculation of explicit trajectories.

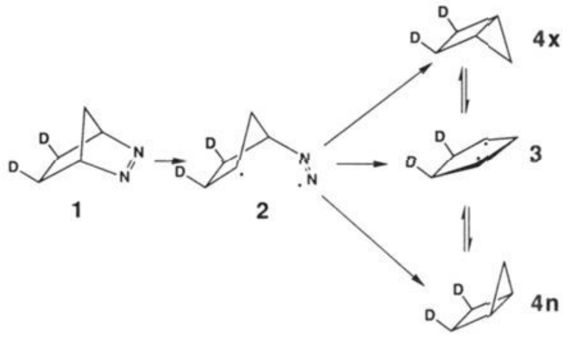

Figure 1.

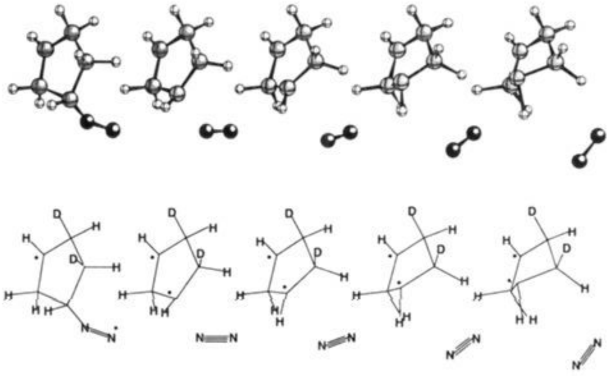

Figure 2. Pictorial representation of the reaction coordinate for N_2 loss from the diazenyl biradical **2**. Based on an AM1 CI frequency calculation on the transition state.

Molecular orbital calculations[5] were carried out on the transition state for nitrogen loss from **2**. The vibrational analyses that were part of these computations revealed, as required, a single imaginary frequency for **2**. The normal vector associated with this imaginary frequency could be translated into a pictorial representation of the reaction coordinate by adding multiples of the elements of the vector to the Cartesian coordinates of the transition structure. This is illustrated in Figure 2 for an AM1 CI calculation on the singlet state of **2**. UHF/6-31G* calculations on the triplet yielded a picture that looks virtually identical.

A striking feature of Figure 2 is the conformational change occurring in the hydrocarbon fragment as the nitrogen departs. *This is a purely dynamic phenomenon*; according to the calculations, the reaction coordinate for nitrogen expulsion "imprints"

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on the hydrocarbon fragment a set of atomic motions that carries it to a part of the potential energy hypersurface where the arrangement of atoms is closer to the structure of **4x** than **4n**. For the triplet state, which requires a spin change before product formation can occur, such dynamic events may be of little consequence, but for the singlet biradical, which could presumably collapse to products very rapidly, the dynamics might provide an explanation for the experimentally observed preference for formation of **4x** over **4n**. This picture is supported by the previous trajectory calculations.[4]

The pictorial representation of the reaction dynamics can be translated into a semiquantitative prediction of the product ratio.[6] The Cartesian atomic displacements corresponding to the reaction coordinate represent the elements of a $3N$-dimensional vector (where N is the number of atoms). We hypothesize that the product ratio can be estimated by comparing components of the mass-weighted reaction coordinate vector along directions leading to post-transition-state minima on the potential energy hypersurface (in the case of **2** these minima would correspond to the two products, **4x** and **4n**, and to cyclopentane-1,3-diyl-*cis*-4,5-d_2 (**3**), which is presumed to lead in turn to **4x** and **4n** with equal probability). This is accomplished by taking dot products with normalized transformation vectors that describe conversion of the transition state into the structures at the subsequent potential energy minima.[7] A first approximation to the requisite transformation vectors comes from mass-weighting a vector derived by taking the difference in x, y, and z coordinates of corresponding atoms in the transition structure and in each of the structures **3**, **4x**, and **4n**.[7] The need to conserve total translational and rotational momentum defines the orientation in space of each of the post-transition-state structures. The problem with transformation vectors defined in this way is that they correspond to linear synchronous transit (LST) reaction paths, which are generally unrealistic representations of the true paths. Thus, in order to accommodate curvature in the reaction paths, a short step down each LST path was used as a starting point for a subsequent geometry optimization.[8] Unit vectors in the directions of these reoptimized points were then used in the dot-product calculations. The results from the AM1 CI calculations are as follows: for azo compound **1**, the calculated k_i/k_r ratio[6] is 4.3 and the observed value is 4.9 ± 0.9; for 2,3-diazabicyclo[2.1.1]hex-2-ene-*exo*-5-d,[9] the calculated value is 1.9 and the observed value is 1.2.[10]

We have also measured an isotope effect on the product ratio for 2,3-diazabicyclo[2.2.1]hept-2-ene by comparing k_i/k_r for **1** and for 2,3-diazabicyclo[2.2.1]hept-2-ene-*endo,endo*-1,4,5,6,7,8-d_6. The calculated isotope effect, defined as $k_i(d_2)k_r(d_6)/k_i(d_6)k_r(d_2)$, is 1.099, and the measured value[11] is 1.10 ± 0.04 (95% confidence interval for four measurements).

It appears that the model presented here can give reasonable results even from relatively low-level (and hence inexpensive) molecular orbital calculations, perhaps because it makes its predictions on geometric rather than energetic grounds.

Acknowledgment. We thank Professor Charles F. Wilcox for helpful discussions.

Supplementary Material Available: A fully annotated Fortran 77 source code listing of the program for computation of transformation vectors and their dot products with a reaction coordinate vector including sample input and output files (11 pages). Ordering information is given on any current masthead page.

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(6) Since the bicyclo[2.1.0]pentane label isomers interconvert under the reaction conditions, it is actually more precise to use a ratio of phenomenological rate constants for inversion and retention (k_i/k_r) than to use the product ratio as an experimental measure to be compared with the calculations.

(7) Since it is the direction of these transformation vectors rather than their length that is of importance, they are normalized prior to mass weighting.

(8) The LST vector is defined by taking differences in Cartesian coordinates for corresponding atoms in the transition state and the post-transition-state minimum. A scalar multiple (<1) then defines the length of the step down this path. The structure resulting from a short step (scalar multiple typically 0.3) is subjected to geometry reoptimization with a single constraint (in the present cases, distance between the nominal radical carbon atoms), using the optimization routine of the molecular orbital program being employed.

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(10) In the computational model as applied to **1**, approximately 83% of **4x** and 26% of **4n** are formed without passing through the cyclopentane-1,3-diyl intermediate. For 2,3-diazabicyclo[2.1.1]hex-2-ene-*exo*-5-d, the corresponding percentages are 80% and 60%.

(11) In presentation of this work at the ACS meeting in New York (August 1991), the measured value was erroneously reported by one of us (B.K.C.) to be 1.88. This error was due to misassignment of a nuclear magnetic resonance.

New Trialkylsilyl Enol Ether Chemistry. Direct β-Azido Functionalization of Triisopropylsilyl Enol Ethers

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The direct conversion of a saturated ketone into a β-functionalized derivative can only be achieved through the intermediacy of an α,β-unsaturated ketone, followed by conjugate addition of a nucleophile (Scheme I). Here we report the unprecedented single-step transformation of a triisopropylsilyl enol ether into a β-azido triisopropylsilyl enol ether.

Treatment of a suspension of iodosobenzene in dichloromethane with trimethylsilyl azide (2.0 equiv) at −78 °C followed by warming to −45 °C gives what is presumed to be the bis-azido adduct **2**.[1] If this solution is warmed to 0 °C, it cleanly decomposes to iodobenzene, nitrogen, and hexamethyldisiloxane [$(Me_3Si)_2O$] (Scheme II).

Addition of the triisopropylsilyl enol ether **3** to a dichloromethane solution of **1**/**2** at −45 °C gave two products, **4** and **23** (90%, 1:1). Reduction of the mixture of **4** and **23** with $LiAlH_4$/ether at 0 °C and workup with *p*-toluenesulfonyl chloride gave the known sulfonamides **24** and **25**.[2] To further conclusively confirm the structure of **4** the 2-naphthylsulfonamide derivative **26** gave crystals that were suitable for single-crystal X-ray crystallography.[3] If the reaction of **1**/**2** with **3** is carried out in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (BMP) at −45 °C, the β-adduct **4** becomes the major product (ca. 4:1). However, addition of trimethylsilyl azide to a suspension of iodosobenzene and the triisopropylsilyl enol ether **3**, at −18 °C to −15 °C (no pyridine), rapidly (15 min) gave the β-azido triisopropylsilyl enol

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(1) For the decomposition of Me_3SiN_3/PhIO to dinitrogen, iodobenzene, and hexamethyldisiloxane, see: Zefirov, N. S.; Safronov, S. O.; Kaznacheev, A. A.; Zhdankin, V. V. *Zh. Org. Khim.* **1989**, *25*, 1807; **1990**, *26*, 1633. Arimoto, M.; Yamaguchi, H.; Fujita, E.; Ochiai, M.; Nagao, Y. *Tetrahedron Lett.* **1987**, *28*, 6289. These authors reported that treatment of allyltrimethylsilanes with $PhIO/Me_3SiN_3/BF_3{\cdot}OEt_2$ gives allyl azides. Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Hopkins, T. E. *Tetrahedron* **1988**, *44*, 1603. β-Diketones react with a $PhIO/Me_3SiN_3/CHCl_3$ reflux to give α-azido β-diketones. Cycloalkenes react with $PhI(OAc)_2/Me_3SiN_3$ to give α-azido ketones; dihydropyran undergoes ring cleavage. Ehrenfreund, J.; Zbiral, E. *Liebigs Ann. Chem.* **1973**, 290. For reviews of PhIO derivatives in organic synthesis, see: Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. Varvoglis, A. *Synthesis* **1984**, 709. Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. Merkushev, E. B. *Russ. Chem. Rev.* **1987**, *56(9)*, 826.

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(3) While the chemical correlation of **4** with **24** is good evidence for the correct structure assignment, the structure of **24** is only based on ^1H and ^{13}C NMR spectroscopy. Given the unusual nature of this transformation, we felt that it was prudent to unambiguously confirm the structural assignment by X-ray crystallography on the derivative **26**.