

disulfide link are not known at this time, but radical intermediates are suspected for the following reasons. (1) The formation of compound **5** by halogen abstraction from the solvent is a process characteristic of reactions involving radicals.¹³ (2) Oxidation of organometallic complexes containing thiolato ligands has been observed to yield complexes containing dialkyl disulfide and diaryl disulfides, presumably via radical intermediates.¹⁶ The novel photoassisted ring opening and coupling that we have described here provides further evidence of the rich reaction chemistry of thietane molecules in polynuclear metal complexes. The ring opening of sulfur-containing heterocycles is believed to be a key step in their desulfurization.¹⁷

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: ORTEP diagrams of the molecular structures of compounds **1-5** and tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for compounds **1-6** (54 pages); tables of observed and calculated structure factors for **1-6** (87 pages). Ordering information is given on any current masthead page.

(16) (a) Treichel, P. M.; Rosenheim, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 691. (b) Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68.

(17) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394. (c) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11. (d) Prins, R.; De Beer, V. H. H.; Somorjai, G. A. *Catal. Rev. Sci. Eng.* **1989**, *31*, 1.

Experimental and Theoretical Investigation of the Inversion of Configuration during Thermal Nitrogen Loss from 2,3-Diazabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-*d*₂

Barbara A. Lyons, Jörg Pfeifer, and Barry K. Carpenter*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853-1301

Received August 19, 1991

The puzzling preference for stereochemical inversion during thermal formation of bicyclo[2.1.0]pentane-2,3-*d*₂ from 2,3-diazabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-*d*₂ (**1**), discovered by Roth and Martin nearly 25 years ago, is still not clearly understood.¹ Recently evidence for the involvement of a diazenyl biradical has been reported.² This communication suggests a theoretical model for the reaction and reports experiments designed to test it.

The lack of a measurable equilibrium isotope effect on the epimerization of bicyclo[2.1.0]pentane-*cis*-2,3-*d*₂³ permits evaluation of the intrinsic rate constants for inversion and retention of configuration during nitrogen extrusion (k_i and k_r , respectively) from the analytical integrated rate equations (see Figure 1 for gas-phase results). The experimental uncertainties (95% confidence interval, including covariances) become relatively large when propagated into k_i/k_r ; nevertheless, application of an F test reveals no significant temperature dependence in the ratio.⁴ This result renders improbable any mechanistic explanation relying on two

(1) (a) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1. (b) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695. For related studies see: (c) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 7133. (d) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 6766.

(2) Simpson, C. J. S. M.; Wilson, G. J.; Adam, W. *J. Am. Chem. Soc.* **1991**, *113*, 4728. See also: Adams, J. S.; Burton, K. A.; Andrews, B. K.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1986**, *108*, 7935. Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115.

(3) Baldwin, J. E.; Ollerenshaw, J. J. *Org. Chem.* **1981**, *46*, 2116.

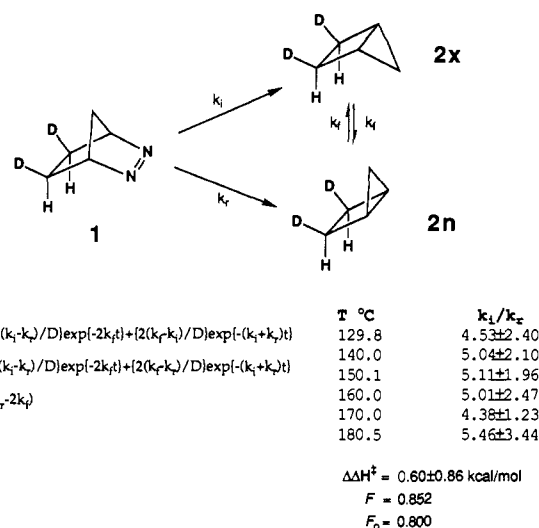


Figure 1. Temperature dependence of the ratio of intrinsic rate constants for inversion and retention of configuration during nitrogen extrusion from the title compound. See ref 4 for an explanation of $\Delta\Delta H^\ddagger$, F , and F_0 .

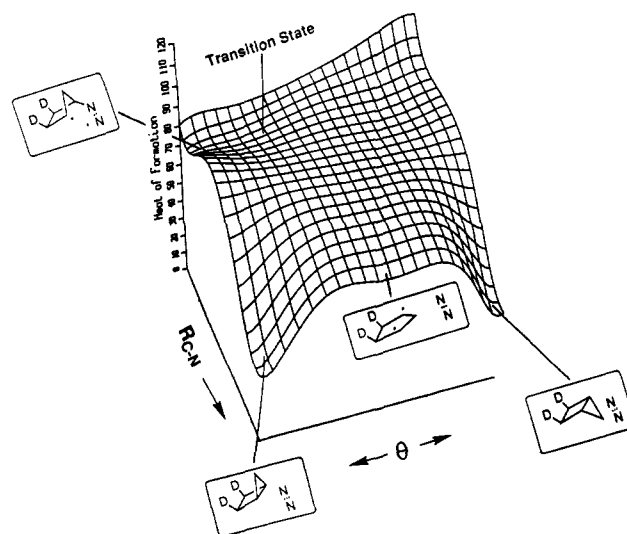


Figure 2. Semiempirical enthalpy surface for the title reaction. R_{C-N} is the length of the C-N bond in the diazenyl biradical. θ is the angle between planes defined by the three- and four-membered rings of bicyclo[2.1.0]pentane. Heats of formation are in kcal/mol.

different transition states for formation of **2x** and **2n**, since the two hypothetical transition states would then have to have coincidentally equal heats of formation (despite presumably significantly different geometries).

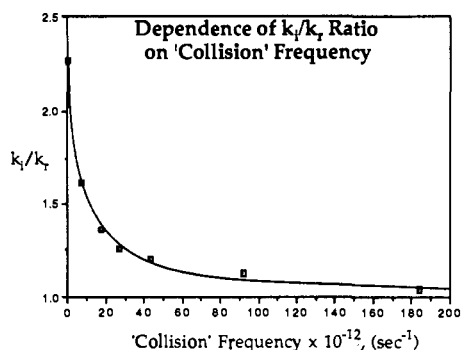
The mechanism we prefer involves branching to the two products and to the cyclopentane-1,3-diyl biradical *after* a single transition state for nitrogen loss from the diazenyl biradical (Figure 2).

When classical trajectory calculations were run on a model surface for this mechanism,⁵ k_i/k_r was calculated to be 2.30 at 130 °C and 2.22 at 180 °C. The agreement with experiment is

(4) F is the ratio of variance of the data for a temperature-independent model, in which k_i/k_r was set equal to a constant, to that for a temperature-dependent model in which the rate constant ratio was assumed to be described by the formula

$$k_i/k_r = \exp(-\Delta\Delta H^\ddagger / RT) \exp(\Delta\Delta S^\ddagger / R)$$

(See, for example, ref 7.) F should be > 1 if k_i/k_r is temperature dependent and < 1 if it is temperature independent. The lower limit of F in the latter case is given by $F_0 = (N - 2)/(N - 1)$, where N is the number of temperatures studied.



	trans-Decalin	cis-Decalin	Dibenzyl ether		
T °C	k _i /k _r	T °C	k _i /k _r		
129.7	1.96±0.10	129.7	1.73±0.13	130.8	1.69±0.07
140.2	2.05±0.06	140.2	1.79±0.05	140.0	1.77±0.14
149.8	2.12±0.11	150.3	1.70±0.12	150.5	1.61±0.37
161.8	2.06±0.09	161.8	1.88±0.07	159.8	1.66±0.06
170.5	2.03±0.09	170.5	1.80±0.12	170.1	1.77±0.34
186.5	2.22±0.22	180.3	1.76±0.13	176.0	1.76±0.13
				182.5	1.71±0.28
ΔΔH [‡]	0.56±0.38	0.24±0.24	0.16±0.23		
F	0.859	0.821	0.836		
F ₀	0.800	0.800	0.833		

Figure 3. Theoretical (graph) and experimental (table) results for the reaction run in solution. See ref 4 for the explanation of $\Delta\Delta H^\ddagger$, F , and F_0 .

fair, reproducing the preference for inversion and the lack of temperature dependence of k_i/k_r (within our experimental error) but not fitting the observed ratio quantitatively. The preference for inversion was found to be due to the planarization at the carbon to which nitrogen is attached, as the nitrogen departs from the diazenyl biradical. This set of atomic motions favors trajectories leading from the transition state to **2x** because of the requirement for conservation of momentum.⁶

The effect of running the reaction in solution was simulated by adding a randomizing component to the trajectories, in the form of pseudocollisions with an adjustable average frequency. The k_i/k_r ratio was calculated for a range of frequencies of these "collisions" (graph in Figure 3). This simulation suggested that, while a reduction in the k_i/k_r value should be expected for reactions in solution, impossibly high "collision" frequencies would be needed to erase the preference for inversion completely.

Experimentally k_i/k_r was determined in three solvents. Reasonable agreement with the theoretical expectations was found (table in Figure 3).

The difference in k_i/k_r between *cis*- and *trans*-decalin is significant within a 97% confidence interval (one-way ANOVA test⁷). We hypothesize that, since vibrational energy exchange in polyatomic liquids appears to occur primarily by a V-V mechanism,⁸ the lower ratio in *cis*-decalin might reflect the higher density of

vibrational states available in a solvent consisting of more flexible molecules with larger numbers of low-frequency vibrations.⁹

In summary, the combined application of theoretical and experimental techniques appears to favor a dynamic explanation for the stereochemical preference in the title reaction. The resulting picture is quite similar to that proposed by Freeman, Pucci, and Binsch for a related reaction.¹⁰

(8) Oxtoby, D. W. *Adv. Chem. Phys.* **1981**, *47* (part 2), 487 and references therein.

(9) The dependence of the ratio of exo:endo products on the reaction medium has been seen previously (Osowski, H. J., dissertation, Ruhr-Universität, Bochum, 1984) but the k_i/k_r ratio could not be determined from this work since no correction for epimerization of the products was applied.

(10) Freeman, J. P.; Pucci, D. G.; Binsch, G. *J. Org. Chem.* **1972**, *37*, 1894.

A Selectivity Control Element for Palladium-Catalyzed Trimethylenemethane Cycloaddition

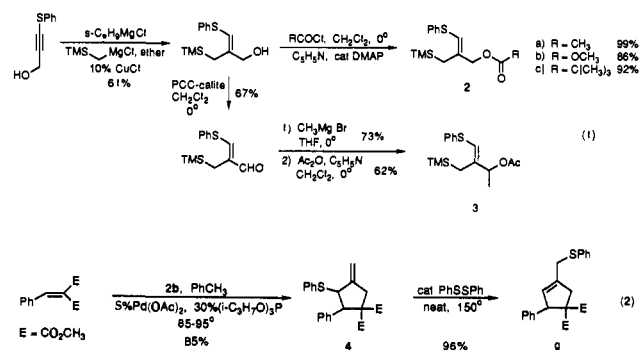
Barry M. Trost* and Michael C. Matelich

Department of Chemistry, Stanford University
Stanford, California 94305-5080

Received July 29, 1991

The utility of synthetic reactions depends upon the ability to direct formation of a desired regio- and diastereoisomer. Introduction of such control in Pd-catalyzed trimethylenemethane (TMM) [3 + 2], [4 + 3], and [6 + 3] cycloadditions will expand their utility in general ring-construction methodology.¹ We record that, contrary to the expectation that a sulfur substituent will be a catalyst poison, a phenylthio group serves as an effective selectivity control element especially when used with 2,4-bis[(4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yl)oxy]pentane (**1**)² as an exceptional new ligand.

The requisite bifunctional conjunctive reagents are prepared as outlined in eq 1.^{3,4} For the carbocuprations, use of the chloride salts and ether as solvent proves important. Equations 2-6 illustrate a cycloaddition with each major class of acceptor.⁵⁻⁹ The



(1) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. Also see: Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77.

(2) Szalontai, G.; Bakos, J.; Toth, I.; Heil, B. *Magn. Reson. Chem.* **1987**, *25*, 761. Lucas, H. J.; Mitchell, F. W., Jr.; Scully, C. N. *J. Am. Chem. Soc.* **1950**, *72*, 5491. White, D. W.; Bertrand, R. D.; McEwen, G. K.; Verkade, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 7125.

(3) Cutting, I.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1209.

(4) Foulon, J. P.; Bourgain-Commerçon, M.; Normant, J. F. *Tetrahedron* **1986**, *42*, 1389.

(5) For enoates, etc., see: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315.

(6) For aldehydes, see: Trost, B. M.; King, S. A.; Schmidt, T. *J. Am. Chem. Soc.* **1989**, *111*, 5902.

(7) For imines: Marrs, C., unpublished observations in these laboratories.

(8) For pyrones, see: Trost, B. M.; Schneider, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 213.

(9) For tropones, see: Trost, B. M.; Seoane, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 615.

(5) Relative heats of formation for the key species were assumed to be equal to relative heats of formation, which came from the following: (i) Turner, B. B.; Goebel, P.; Mallon, B. J.; Doering, W. von E.; Coburn, J. F.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315. (ii) Reference 3. (iii) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (iv) Engel, P. S.; Wood, J. L.; Sweet, J. A.; Margrave, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 2381. (v) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3033. Other points were determined by AM1 calculation (Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902) or Benson group additivity (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976). A polynomial interpolation function was used.

(6) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1985**, *107*, 5730. (b) Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* **1990**, *55*, 695.

(7) Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 2nd ed.; Ellis Horwood Ltd.: Chichester, 1988.