Table I. Isotropic Shifts for $Co(AA)_2(4,7\text{-phen})$ in $CDCl_3$[a]

Position	303°K	263°K	223°K	203°K
2,9-H	−56.10	−51.35	−38.00	−27.70
3,8-H	−19.67	−23.80	−30.05	−33.80
4,7-CH_3	+10.23	+12.06	+14.62	+16.33
5,6-H	−23.66	−25.50	−27.00	−27.40
AA-CH	+23.25	+26.26	+28.02	+30.10
AA-CH_3	−11.47[b]	−13.65[b]	+2.54	+2.36
AA-CH_3			−40.72	−45.92

[a] Shifts in ppm at 100 MHz, referenced against diamagnetic ligand. [b] Averaged proton nmr signal.

ture. Whether this anomaly is related to the nature of the transition state in the form of a temperature-dependent equilibrium between octahedral and five-coordinated species is not known at this time. The two species would be expected to exhibit very different isotropic shift patterns. Alternatively, the thermally accessible Kramers doublets for the octahedral complex[13] may possess widely differing magnetic anisotropies, so that varying the temperature alters the population of the accessible states. This latter mechanism has been predicted[10,13] and observed[14] for some six-coordinated Co(II) chelates.

A more extensive investigation into solvent and substituent effects in progress should shed further light on the mechanism of this rearrangement and on the origin of the non-Curie behavior of the shifts.

(13) J. P. Jesson, *J. Chem. Phys.*, 47, 582 (1967).
(14) G. N. La Mar and J. P. Jesson, unpublished data.

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Chemistry of Bicyclo[5.1.0]oct-2-yl Cations

Sir:

Much research has been done to determine the structure(s) of the minimum energy conformation(s) of various substituted cyclopropylcarbinyl cations. Product studies in the bicyclo[*n*.1.0]alk-2-yl systems (*n* = 3–4)[1b-c] indicate that there is only one conformationally stable interaction of the electron-deficient p orbital with the cyclopropane ring. We wish to report the solvolytic chemistry of *endo*- and *exo*-bicyclo[5.1.0]oct-2-yl 3,5-dinitrobenzoates (**1a,b**) in which, by contrast, a minimum of two structurally distinct cations are formed as intermediates.

The results of our product studies are given in Table I. The slightly differing product distribution from the two solvolyses is similar to that observed by Cope[1d] in acetic acid solution and provides evidence for at least two intermediate cations. We do not wish to stress any importance to these results, however, be-

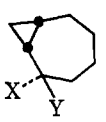
(1) (a) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *J. Amer. Chem. Soc.*, **90**, 5338 (1968); (b) G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968); P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Commun.*, 425 (1968); (c) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, Abstracts of Paper, p K011; (d) A. C. Cope, S. Moon, and C. J. Park, *J. Amer. Chem. Soc.*, **84**, 4850 (1962); (e) unpublished results of C. D. Poulter, E. C. Friedrich, and S. Winstein, University of California, Los Angeles, Calif.; (f) unpublished results of C. D. Poulter and S. Winstein, University of California, Los Angeles, Calif.

Table I. Products from Solvolysis[a] of *endo*- and *exo*-Bicyclo[5.1.0]oct-2-yl 3,5-Dinitrobenzoates (**1a,b**)

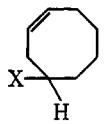
Products	% yield from *endo*-DNB **1a**	% yield from *exo*-DNB **1b**
endo-DNB **1a**	4 (unreacted)	0
exo-DNB **1b**	6	13 (unreacted)
Δ^3-DNB **2a**[c]	6	2
endo-OH **1c**[c]	47 (56)[b]	44 (52)[b]
exo-OH **1d**[c]	16 (19)[b]	30 (35)[b]
Δ^3-OH **2b**[c]	21 (25)[b]	11 (13)[b]

[a] 80% aqueous acetone buffered with 1.1 equiv of lutidine at 100°. [b] Normalized to 100%, standard deviation ±3%. [c] These products were stable to the reaction conditions.

cause kinetic and scrambling studies appear to provide in this system an even more sensitive probe for differing cationic intermediates.



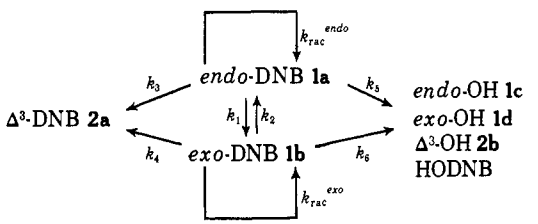
1a, *endo*-DNB; X = DNB; Y = H
b, *exo*-DNB; X = H; Y = DNB
c, *endo*-OH; X = OH; Y = H
d. *exo*-OH; X = H; Y = OH
e, *endo* D-DNB; X = DNB; Y = D
f, *exo*-D-DNB; X = D; Y = DNB



2a, Δ^3-DNB; X = DNB
b, Δ^3-OH; X = OH

Both titrimetric and polarimetric kinetic studies were conducted. The data were analyzed according to Scheme I. The titrimetric study of *endo*-DNB **1a**

Scheme I. Kinetic Scheme for Solvolysis of *endo*- and *exo*-3,5-Dinitrobenzoates **1a,b**



showed slightly curved first-order plots after approximately three half-lives due to slight instability of the small amount of returned *exo*-DNB **1b**. This curvature was resolved into observed rate constants with a nonlinear iterative regression analysis. Solvolysis of *exo*-DNB **1b** gave good first-order plots.

In the racemization rate studies, the total optical rotation of the solution *vs.* time was measured and observed to follow good first-order kinetics over two half-lives. The quantity, k_{rac}, reported in Table II, was calculated as the difference between k_α^{obsd} and either k_7 or k_8. The values for k_6 were calculated by assuming $k_2 \approx 0$. Even though we believe that k_2 may be as high as 25% of k_8, our data do not distinguish whether products from *exo*-DNB **1b** arise solely from k_6 or partly from k_6 and k_2; under the reaction conditions for the solvolysis of **1b**, **1a** is so reactive that, at best, it can only achieve a steady-state concentration.

We also studied the products from the solvolyses of *endo*-D- and *exo*-D-DNB **1e,f**. After 81% reaction, the alcoholic products and unreacted starting material from *endo*-D-DNB **1e** retained unscrambled deuterium atoms. The results for *exo*-D-DNB **1f** are given in Table III. The per cent racemization of unreacted *exo*-D-

Table II. Rate Constants for Solvolyses[a] of *endo*- and *exo*-Dinitrobenzoates **1a,b**

Temp, °C[c]	Rate constants,[b] $10^5 \times k$, sec^{-1} k_7[d]	k_5[e]	k_{rac}[endo]
	endo-DNB **1a**		
75.73	2.98 ± 0.03	2.52	0.03 ± 0.20
75.73	2.97 ± 0.03	2.58	
83.52	7.55 ± 0.06	6.45	
83.88	7.84 ± 0.17	6.77	
Temp, °C[c]	Rate constants,[b] $10^5 \times k$, sec^{-1} k_8[f]	k_6[g]	k_{rac}[exo]
	exo-DNB **1b**		
100.00	2.14 ± 0.04	2.06	1.65 ± 0.18
100.00	2.27 ± 0.05	2.15	
109.50	4.99 ± 0.07	4.80	
109.50	5.05 ± 0.04	4.88	

[a] Unbuffered 80% aqueous acetone. [b] All errors are standard deviations. [c] Temperature error is ±0.05°. [d] $k_7 = (k_1 + k_3 + k_5)$. [e] $\Delta H^{\ddagger} = 28.9 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = 2.9 \pm 1.1$ eu. [f] $k_8 = (k_2 + k_4 + k_6)$. [g] $\Delta H^{\ddagger} = 24.1 \pm 0.7$ kcal/mol, $\Delta S^{\ddagger} = -15.8 \pm 1.8$ eu.

Table III. Deuterium Scrambling in Solvolysis[a] of *exo*-D-DNB **1f**

Product	% deuterium scrambling[b]
exo-D-DNB **1f** (unreacted)	87.4 ± 0.3
Δ^3-DNB **2a**	83.6 ± 0.5
endo-OH **1c**	94.9 ± 1.1
exo-OH **1d**	98.4 ± 3.3
Δ^3-OH **2b**	90.4 ± 0.6

[a] Lutidine-buffered 80% aqueous acetone at 110° after 93% reaction. [b] Determined by nmr; all errors are standard deviations.

DNB **1f** at 93% reaction can be estimated from Table II. The calculated 87% racemization agrees with the observed scrambling and therefore demands that the mechanisms of racemization and deuterium scrambling are the same, namely, a degenerate cyclopropylcarbinyl rearrangement.

In summary, the results clearly show that the cation(s) or ion pairs from *endo*-DNB **1a** do not scramble or racemize while those from the *exo* system both scramble and racemize. These results are reasonable because the isomer which gives racemization has the cyclopropyl group *trans* to the leaving group. Unfortunately our results do not distinguish between conformationally isomeric bisected cations, bicyclobutonium ions, or other possible sets of intermediate cations. Nevertheless, studies such as we have described should be performed on the other bicyclo[*n*.1.0]alk-2-yl systems (n = 2–7)[1a-f] before firm conclusions can be made. Only the *endo*-bicyclo[4.1.0]hept-2-yl *p*-nitrobenzoate has been studied polarimetrically and gave no racemization.[1c] In light of our results, the failure to study the *exo* system is belatedly a serious one.

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Chemical Evolution of a Nitrogenase Model. I. Reduction of Acetylene and Other Substrates by a Molybdenum–Thiol Catalyst System

Sir:

Two of the most remarkable features of the nitrogenase enzyme of *Clostridium pasteurianum*, *Azotobacter vinelandii*, and other microbial nitrogen-fixing systems are the nonspecificity with regard to substrates that can be reduced and the ease with which acetylene is reduced to ethylene but not to ethane.[1] For this reason Hardy introduced acetylene as a convenient substrate for assaying nitrogenase activity.[2] Acetylene is a competitive inhibitor of N_2 fixation and is believed to be bound to the same active site.

In this communication we wish to report results of experiments performed toward the goal of developing plausible, catalytic nitrogenase model systems. The nitrogenase of *C. pasteurianum* consists of an "electron-activating system," which is ATP dependent, and the actual nitrogenase.[1] The active site is believed to contain molybdenum, nonheme iron, and labile sulfhydryl groups. In the absence of substrates the holoenzyme catalyzes hydrogen evolution.[1]

To develop an initial catalytic, nonprotein model for nitrogenase, we have approximated the active site with thiol complexes of transition metals, and the electron donor pool by reducing agents such as $NaBH_4$, $Na_2S_2O_4$, $NaBH(OCH_3)_3$, Na_2SnO_2, sodium ascorbate, metallic Zn, or Al. Table I shows the relative activity of various transition metals as catalysts for the reduction of acetylene to ethylene in an aqueous, alkaline solution containing thiol and excess $Na_2S_2O_4$.[3] While not the most vigorous reducing agent of those described above, sodium hydrosulfite was employed for this study because of its demonstrated ability as a reductant for the enzyme system.[1]

Table I. Relative Activities of Transition Metals in the Reduction of Acetylene to Ethylene at 27° [a]

Metal	Rel activity[b]	Metal	Rel activity[b]	Metal	Rel activity[b]
Ti	0	Y	0	Hf	...[c]
V	0	Zr	0	Ta	0.1
Cr	0	Nb	0.1	W	0
Mn	0	Mo	100.0	Re	0.1
Fe	0	Tc	...[c]	Os	0.1
Co	0	Ru	2.9	Ir	15.5
Ni	0	Rh	0.4	Pt	0.1
Cu	0	Pd	1.3	Au	0
Zn	0	Ag	0	Hg	0

[a] Reaction conditions: reaction solutions containing 1 mmol of transition metal salt (mostly chloride), 1 mmol of 1-thioglycerol, 2 mmol of $Na_2S_2O_4$, and 10 mmol of NaOH in 10 ml of H_2O were placed into glass vials of 15-ml volume and were sealed with rubber serum caps. The air was then replaced by water-washed acetylene at 1 atm of pressure. Relative rates are reported for 16-hr reaction periods. [b] Relative rate of Mo = 100.0. [c] Not determined.

The remarkable specific activity of molybdenum is one of the salient features of our system. Of all the

(1) (a) R. W. F. Hardy and R. C. Burns, *Ann. Rev. Biochem.*, **37**, 331 (1968), and references cited therein; (b) K. Kuchynka, *Catalysis Rev.*, **3**, 111 (1969), and references cited therein.

(2) R. W. F. Hardy and E. Knight, Jr., *Biochim. Biophys. Acta*, **139**, 69 (1967).

(3) When $NaBH_4$ is used as the reducing agent, hydrogen evolution is observed at neutral or mildly alkaline pH. Thus, our model system also catalyzes hydrogen evolution.