The Rh is octahedrally coordinated. Four positions are taken up by the porphyrin pyrrole nitrogen atoms (Rh–N average distance 2.04 Å); a chloride ion (Rh–Cl distance of 2.35 Å) and a phenyl group that is σ-bonded to the Rh (Rh–C distance 2.05 Å); complete the coordination. The phenyl group is approximately perpendicular to the mean porphyrin plane.

The mechanism of formation and chemistry of this interesting species is presently under investigation.[23]

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(24) Alfred P. Sloan Fellow.

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Thermolysis of *exo*- and *endo*-5-Methoxy-2,3-diazabicyclo[2.2.1]-2-heptene[1]

Sir:

Currently there is great interest concerning the mechanistic details of thermal[2–4] and photolytic[3–8] decomposition of azo compounds. We wish to report our investigation of gas-phase thermal decomposition of the stereomeric bicyclic azo compounds Ix and In.

The necessary syntheses were accomplished by methylation of 2,3-dicarbomethoxy-2,3-diazabicyclo-[2.2.1]-5-heptanols of established 5-*exo* and 5-*endo* configuration[9] with sodium hydride and iodomethane in tetrahydrofuran. These methoxyl derivatives were converted by known procedures[10,11] to Ix, bp 61.5° (4.5 mm), and In, bp 73.5° (2.2 mm). Spectral data and elemental analyses were in complete agreement with the structures.

Thermal decomposition of Ix and In gave the 2-methoxybicyclo[2.1.0]pentanes *cis*-III and *trans*-III as the only products ($>95\%$) under our reaction conditions. Identification is based on nmr spectra. Carbon-13 magnetic resonance spectra allowed for conclusive assignment of configuration. The C-5 carbon of *cis*-III was shifted upfield 5 ppm from the corresponding carbon of *trans*-III and bicyclo[2.1.0]pentane.[12]

For gas-phase decomposition, 5–6-μl samples of azo compound were degassed and sealed in 25-ml Pyrex tubes under nitrogen at *ca.* 0.6 mm. Upon completion of reaction the pressure was <100 mm. Product interconversion was examined under decomposition conditions and at higher temperature with the aid of a 47.9% *cis*-III and 52.1% *trans*-III mixture obtained from photolysis of Ix. Some results are summarized in Table I.

Table I. Thermal Decomposition of Ix and In and Isomerization of Products *cis*-III and *trans*-III

Compd	Temp, °C	% composition[a] *cis*-III	% composition[a] *trans*-III
Ix	135[b]	63.0 ± 0.6	37.0 ± 0.6
Ix	198.9[c]	85.6 ± 0.4	14.4 ± 0.4
Ix	220[d]	85.5 ± 0.4	14.5 ± 0.4
In	135[e]	93.6 ± 0.5	6.4 ± 0.5
In	198.9[c]	85.9 ± 0.5	14.1 ± 0.5
In	220[d]	85.2 ± 0.5	14.8 ± 0.4
47.9% *cis*-III + 52.1% *trans*-III	135[f]	48.9 ± 0.3[g]	51.1 ± 0.3[g]
47.9% *cis*-III + 52.1% *trans*-III	198.9[c]	85.4 ± 0.5	14.6 ± 0.5

[a] Determined with a 20 ft × 0.125 in. 15% tetraethylene glycol on Chromosorb P, gas chromatography column. [b] For five half-lives. [c] For 16 hr. [d] For 5.5 hr. [e] For 2.5 half-lives (100 hr). [f] For 100 hr. [g] Equilibrium composition at 135° is 87.1% *cis*-III and 12.9% *trans*-III as extrapolated from the equilibrium constant data at 198.9 and 220°.

Kinetics of decomposition were followed by gas chromatography by measuring the appearance of combined III against 1,2-dimethoxyethane as an internal standard. A comparison of Ix and In with 2,3-diazabicyclo[2.2.1]-2-heptene (IV) is shown in Table II. Decomposition of *exo*-6-*d*-Ix did not lead to scrambling of the label. This rules out any neighboring group participation by the 5-methoxyl group.

Table II. Kinetics of Ix and In Decomposition at 160.1°

Compd	10^4k, sec^{-1}	Rel rate
IV	0.895[a]	1.0
Ix	5.4[b]	6.0
In	0.80[b]	0.9

[a] Calculated from other reported data.[11] [b] Determined with a 5-ft 15% Carbowax 20M gas chromatography column.

Greatly different product ratios from thermolysis of Ix and In show that a single planar 1,3-diradical intermediate, II, cannot explain the decomposition mechanism. Comparison of decomposition and equilibrium product ratios clearly indicate that net inversion of structure results from each isomer.

Recently Roth and Martin[3] reported an analogous inversion observation. Thermolysis of *exo*-5,6-d_2-IV gave a 75:25 mixture of Va and Vb. These authors attribute inversion to concerted elimination of nitrogen with accompanying back-side p-orbital overlap *via* transition-state VI. However, examination of models casts considerable doubt on this proposal. The geometry required for transition-state VI has diverging orbitals unfavorably oriented for back-side overlap (end view). Furthermore, extended Hückel calculations[2a–c,13] suggest that the developing orbitals will be antisymmetric and "nonbonding." It seems unlikely that such a path will favor inversion.

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(1) This work was supported by the National Science Foundation under Grant GP-6923.

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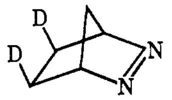
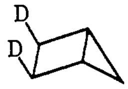
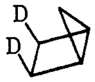
(13) R. Hoffmann, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.



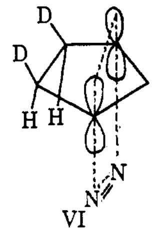
IV



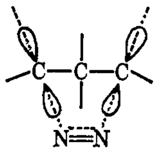
Va



Vb



VI



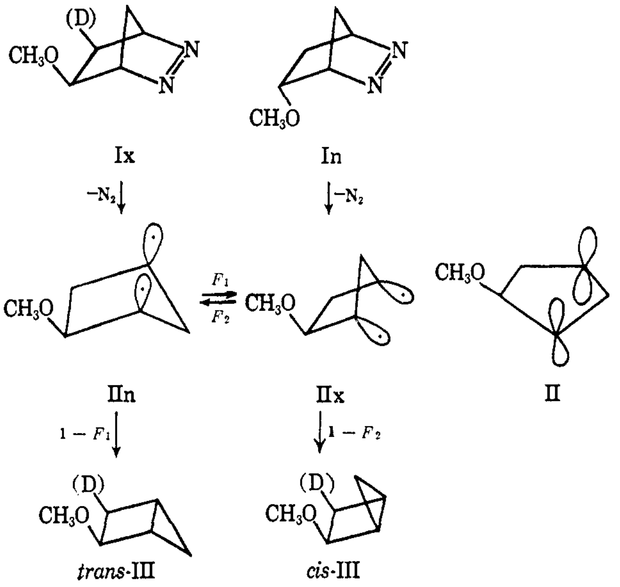
end view

VI

The Ix–In system provides a test of the above mechanism. Consideration of steric interaction between an *exo*-methoxyl group and C-7 hydrogen implies that Ix should show more inversion than IV. An *endo*-methoxyl group should cause hindrance to departure of nitrogen, and less inversion is predicted for In. These expectations are not realized. While the rate increases with Ix, inversion is substantially less. For In the rate decreases, but inversion is significantly greater.

A more plausible mechanism which accounts for the results may be formulated as shown in Scheme I. We propose that structurally inverted pyramidal diradicals IIn and IIx arise directly upon nitrogen elimination for Ix and In, respectively.[14–16] This inversion is thought to be a consequence of recoil from energy released by C–N bond breaking.[17] The excess product of inverted structure indicates that ring closure occurs before IIn or IIx fully equilibrate. The magnitude of decomposition rate differences strongly suggests that little product of retained structure results by direct formation of structurally retained diradicals from Ix or In.

Scheme I



It is instructive to evaluate the mole fraction of nonplanar diradicals which invert (F) or close to product ($1 - F$). This is accomplished by adjusting the values with successive approximations until both experimental product ratios are reproduced. The best values are $F_1 = 0.672$, $(1 - F_1) = 0.328$, $F_2 = 0.174$, and $(1 - F_2) = 0.826$. These fractions require that IIn and IIx be very short-lived. As calculated from eq 1, the per cent product, P, arising from diradicals which close directly

$$P = 100[(1 - F_1) + F_1(1 - F_2)] = 100[(1 - F_2) + F_2(1 - F_1)] \quad (1)$$

or invert only once and then close is 88.3%. A similar analysis of the *exo*-5,6-d_2-IV data shows 89.0% product formation before the nonplanar intermediates can invert more than once. This correspondence of values serves as a check of Scheme I since the diradicals from the Ix–In system and IV should have comparable lifetimes.

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[14] At present it is not clear whether a planar intermediate, II, also is involved, or if such a conformation only represents a transition state. It seems likely that II will be of higher energy than IIn or IIx because of strain imposed by planar 1,3-carbons in a five-membered ring.

[15] There is precedent for a short-lived nonplanar alkyl radical: P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. F. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965).

[16] Recent results afford ample evidence that thermolysis of other 1-pyrazolines leads to nitrogen-free intermediates.[2a–c]

[17] A referee has suggested that orbital symmetry considerations may offer an explanation for the "direct" formation of inverted diradicals. We had considered this unlikely; a similar opinion has been reached by R. Hoffmann (private communication).

Circular Dichroism and the Absolute Configuration of the Chiral Disulfide Group[1]

Sir:

The S–S group has long been known to prefer a skewed, asymmetric spatial arrangement, whether in H_2S_2,[2] in allotropic forms of elemental sulfur,[3] in some inorganic polythio compounds,[4] or in various organic compounds whose structures have been determined by X-ray and other physical methods. Skewed configurations were predicted[5] for the general case of compounds containing atoms, $-\ddot{\underset{..}{A}}-\ddot{\underset{..}{B}}-$, with unshared electrons on adjacent atoms.

The energy barrier to rotation about the sulfur–sulfur bond has been variously estimated at 3–14 kcal/mole.[6] Enantiomeric forms of simple disulfides would not be expected to be resolvable at room temperature. The presence, however, of a fixed asymmetric center near a disulfide group in a molecule creates the possibility for unequal distribution of diasteroisomeric forms by a kind of asymmetric induction.[7] Fredga[8] has described a number of examples of large optical rotations observed even in the visible region for compounds having a disulfide group near an asymmetric carbon atom.[8]

ORD[9] and CD[10] spectra for cystine and certain cyclic

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[1] Publication No. 1519 of the Department of Chemistry, Indiana University.

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