in that the peaks to be eliminated must have different relaxation characteristics to those which are to be observed. The approach described in this communication and that described by Shaefer[8] (in which the solvent or impurity peak is selectively saturated before each pulse is applied) do not have this limitation. A choice between these latter two methods will depend on the particular system under study.

Of course, unlike the ^{31}P experiment described here, none of the earlier experiments mentioned in the last paragraph are applicable to homonuclear decoupled Fourier transform nmr.

(8) J. Schaefer, *J. Magn. Resonance*, 6, 670 (1972).

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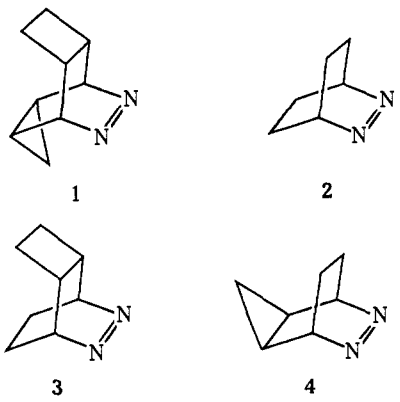
Orientational Effects on Cyclopropyl Participation in the Thermolysis of Azo Compounds. Assessment of the Endo Configuration

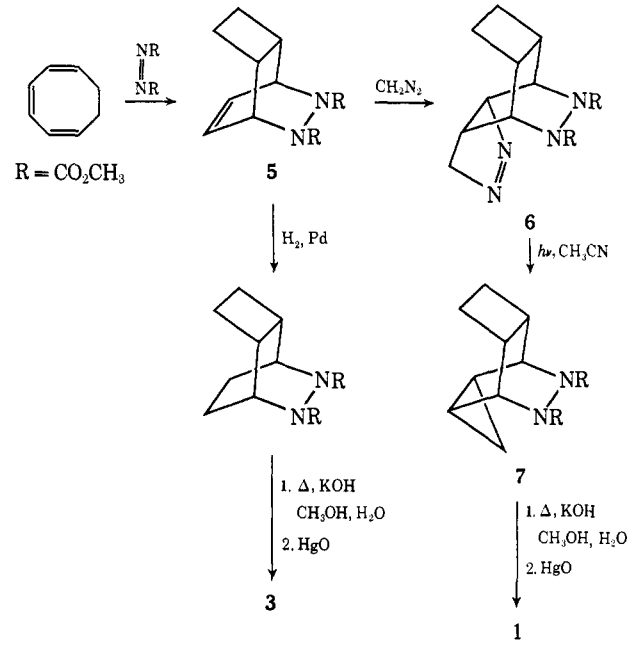
Sir:

Recent thermolysis studies of azo compounds have proven to be uniquely informative about the influence of geometry on the contribution made by edge cyclopropyl electrons to chemical reactivity.[1-3] For the case of the exo configuration,[4] changes in the dihedral angle between the plane of the cyclopropane ring and the rest of the structure produce very substantial differences in reactivity.[1] Surprisingly, there has been no comparison of the reactivities of the endo and exo arrangements. We now report a quantitative assessment of the influence of an *endo*-cyclopropane ring on the thermal reactivity of azo compounds.[5] The structures we use for this purpose are azo compound **1** and the known compounds **2**,[2,6] **3**,[2,7] and **4**.[2]

Scheme I outlines the synthetic sequence used to prepare **1**. Compound **1** is characterized by mp 59.5–60.5° (from dichloromethane–pentane); $\lambda_{max}^{isooctane}$ 383 (ϵ 294) and 372 nm (sh) (ϵ 112);[6] λ_{max}^{KBr} 6.63 μ (–N=N–);[6] and nmr, τ ($CDCl_3$) 10.29 (1 H, overlaid triplets), 9.85 (1 H, overlaid triplets complicated by additional small couplings), 8.44 (2 H, multiplet), 7.96 (6 H, singlet), and 4.94 (2 H, broad singlet).[8] The stereochemistry of the cyclobutane ring in **5**, **6**, **7**, and **1** was shown to be exo by the conversion of **5** into a product which had physical and spectral properties identical with those of



Scheme I



authentic **3**.[2,9] The assignment of the endo configuration to the cyclopropane ring in **1** is supported by three lines of evidence: (a) examination of models clearly shows that diazomethane is blocked from addition to the exo side of the double bond of **5** by the proximate cyclobutyl group; (b) an nmr signal above τ 10 indicates the juxtaposition of this cyclopropyl proton and the azo linkage;[10,11] and (c) an enormous difference in the thermolysis rates of **1** and **4** establishes that the cyclopropyl groups of the two compounds are of different orientations.

The first-order rate constants for the thermolysis of **1** in the range of 177–199° were measured by a previously described method.[6] These results, along with a comparison of reactivity between **1**, **2**, **3**, and **4**,[12] are

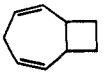
(1) E. L. Allred and A. L. Johnson, *J. Amer. Chem. Soc.*, 93, 1300 (1971).
(2) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969).
(3) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Amer. Chem. Soc.*, 91, 3382 (1969).
(4) The designation exo refers to the relationship between the cyclopropane ring and the –N=N– group.
(5) An *endo*-cyclopropyl azo compound has been decomposed [L. A. Paquette and M. J. Epstein, *J. Amer. Chem. Soc.*, 93, 5936 (1971)]; however, a phenyl group at each C–N carbon and the lack of a corresponding *exo*-cyclopropyl compound precludes any quantitative evaluation of the effect of a cyclopropane ring in the endo configuration.
(6) S. G. Cohen and R. Zand, *ibid.*, 84, 586 (1962).
(7) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 387 (1972).
(8) Products 1 and 6 (mp 133.5–135°) gave satisfactory elemental analyses, and all compounds gave spectral data in accord with their assigned structures.
(9) R. C. Cookson, S. S. H. Giliani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967); A. B. Evnin, R. D. Miller, and G. R. Evanega, *Tetrahedron Lett.*, 5863 (1968).
(10) This cyclopropyl proton signal is at least 0.4 ppm upfield from any cyclopropyl proton of **4**: M. Martin and W. R. Roth, *Chem. Ber.*, 102, 811 (1969).
(11) The shielding effect of the –N=N– structure is well established. For example, see : (a) J. J. Uebel and J. C. Martin, *J. Amer. Chem. Soc.*, 86, 4618 (1964); (b) R. J. Crawford, A. Mishra, and R. Dummel, *ibid.*, 88, 5959 (1966); (c) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, 702, 1 (1967).
(12) This comparison necessitates extrapolation of the kinetic data between gas- and liquid-phase conditions. Previous control experiments have demonstrated that the decomposition rates of such azo compounds are not appreciably greater in solution than in the gas phase.[1,2]

Table I. Thermolysis Rate Data for Some Selected Azo Compounds

Compd	Temp, °C	10^4k, sec^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate
1	+176.9	0.35			
	+189.0	1.14			
	+199.2	3.32	41.4 ± 0.3	+10.3	
	−3.5[a]	1.32×10^{-14}			8.8×10^2
2[b]	+240.0	212	44.6 ± 0.2	+10.5	
	−3.5				1
3[c]	+150.2	0.3	39.2 ± 0.3	+11	
	−3.5				6.7×10^4
4[c]	−3.5	1.71	14.9 ± 1.5	−21	1.1×10^{17}

[a] Extrapolated to −3.5° from the data at higher temperatures.[12] [b] Taken from ref 2 and 6. [c] Taken from ref 2.

summarized in Table I. Decomposition of **1** at 180° gave a product mixture consisting of 86% bicyclo[5.2.0]nona-2,5-diene (**8**)[13] and 14% of five other compounds.[14]



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The striking feature of the data in Table I is that decomposition of **4** is accelerated over that of **1** by $>10^{14}$. This represents one of the largest, if not the largest, rate factor yet observed between the two cyclopropyl configurations.[15-17] All available criteria clearly indicate that **1** decomposes by a diradical pathway without participation by the cyclopropane ring.[1-3,10,11c,18-21] It is evident from structural considerations that the changeover in mechanism which occurs in going from **4** to **1**[2,10] is a consequence of the differences in transition-state stereochemistry resulting from disrotatory opening of the edge cyclopropyl orbitals.[22] Models of the transition states based on "outward" rotation of participating cyclopropyl electrons clearly show perfectly aligned overlapping orbitals for the enormously accelerated **4** but orthogonally oriented orbitals with little or no overlap for **1**.[22] Participation with "inward" rotation of the cyclopropyl orbitals of **1** is improbable since it would lead to a severely strained transition state and a *trans,trans*-cycloheptadiene as product.[22] The results with **1** and **4** add an important calibration point to the evaluation of the influences of *endo*- and *exo*-cyclopropane orientations on chemical reactivity.

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Absolute Configuration of 1-Oxo[2.2]metacyclophane

Sir:

The stereochemistry of [2.2]metacyclophanes has attracted considerable attention.[1] We now wish to report the first absolute configurational assignment to a member of this family of compounds, 1-oxo[2.2]-metacyclophane (**1**).[2]

The long-wavelength spectral region of (−)-**1** (Figure 1) is dominated by an intense negative Cotton effect

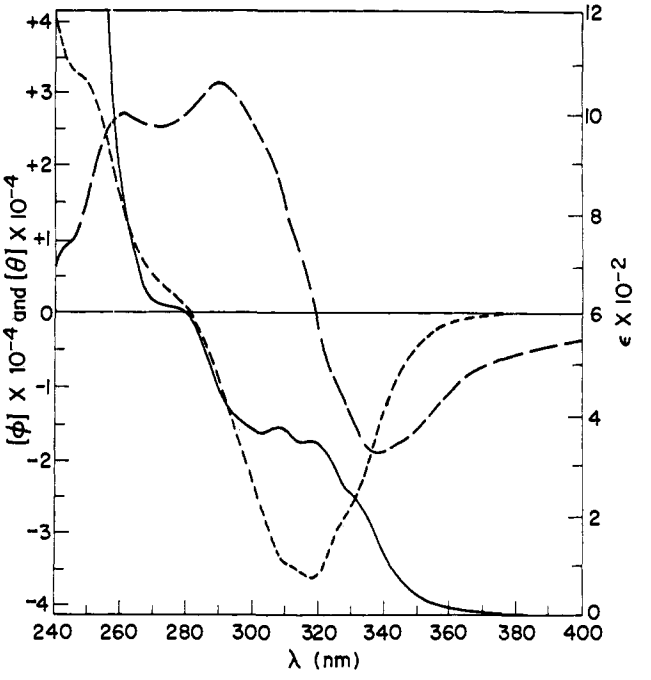

Figure 1. Spectral properties of (−)-1-oxo[2.2]metacyclophane (**1**) in isooctane solution: solid line, absorption spectrum (ordinate scale on the right); short dashes, circular dichroism; long dashes, optical rotatory dispersion (ordinate scale for the chiroptical properties on the left).

centered near 318 nm, which corresponds to the lowest lying n → π* carbonyl transition (the R band) at 310–330 nm. The high rotational strength of this transition ($[\theta]_{max}$ −36,700°) is in contrast to the relatively weak isotropic absorption, $\epsilon \sim 100$ (after subtraction of the absorption tail).[3]

(13) W. R. Roth, *Justus Liebigs Ann. Chem.*, 671, 10 (1964).
(14) The five products were present in approximately equal amounts. They have not been identified as yet because of the limited quantities available.
(15) The 10^2 reactivity difference between **1** and **3** suggests that the factor may be at least 10^{16}.
(16) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, 91, 3020 (1969); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, 89, 1954 (1967); H. Tanida, T. Tsuji, and T. Irie, *ibid.*, 89, 1953 (1967); R. M. Coates and J. L. Kirkpatrick, *ibid.*, 92, 4883 (1970).
(17) S. C. Clarke and B. L. Johnson, *Tetrahedron*, 27, 3555 (1971); B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Amer. Chem. Soc.*, 89, 5964 (1967).
(18) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, 48, 628 (1970); R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, 88, 3963 (1966); and other papers in the series.
(19) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967).
(20) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, 91, 6766 (1969).
(21) J. A. Berson and S. S. Olin, *ibid.*, 91, 777 (1969).
(22) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 38–48.

(1) For a recent review, see F. Vögtle and P. Neumann, *Angew. Chem., Int. Ed. Engl.*, 11, 73 (1972).
(2) H. W. Gschwend, *J. Amer. Chem. Soc.*, 94, 8430 (1972).
(3) Also evinced in Figure 1 are two weakly positive Cotton effects at 280 and 250 nm. In addition, two strongly active transitions are centered at shorter wavelengths: a positive Cotton effect at 231 nm ($[\theta]_{max}$ +63,100), and a negative Cotton effect at 207 nm (molecular amplitude (a) ~ −3600) corresponding to the strong absorption at 207 nm (ϵ 40,700).