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THERMAL STABILITY OF CIS-OXADIAZIRIDINES.
AN EXAMPLE OF ANCHIMERICALLY ASSISTED RING OPENING.

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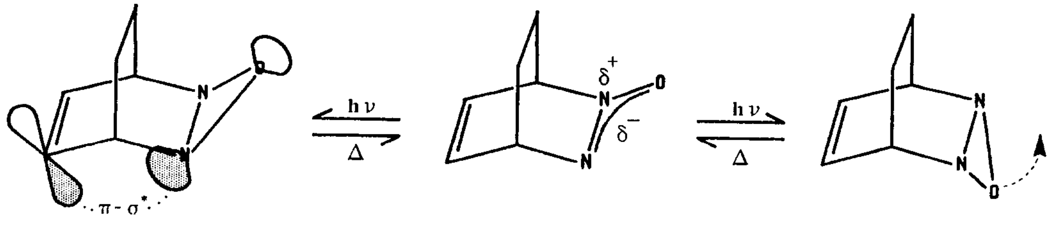
Abstract: The thermal decay of oxadiaziridines (ODZs) photochemically generated from a series of bicyclic azoxy compounds is examined. The thermal reversion of exo ODZs to the starting azoxy compounds shows a significant rate enhancement. These reactions appear to be examples of anchimeric assistance by homoallylic π bonds involving only neutral species.

Participation of π bonds in displacement reactions of bicyclic systems has been of interest since Roberts first reported a difference in the solvolysis rates for exo and endo norbornenyl halides.[1] We wish to report an interesting example of such π bond participation in the thermal reversion of the oxadiaziridine (ODZ) photoproducts of unsaturated cyclic (cis) azoxy systems. This reversion is a rare example of π bond participation involving only neutral species.

Photolysis[2] at -78°C of 2,3-diazabicyclo[2.2.2]octa-2,5-diene N-oxide (**I**)[3] in CD_2Cl_2 establishes a photostationary state with two photoproducts. These products are the exo (**II**) and endo (**III**) ODZ isomers[4] as determined by low temperature NMR (Table 1). Photoequilibria between azoxy and ODZ moieties have previously been observed in acyclic azoxy systems,[5] and by Michl[6] and Olsen[7] for similar bicyclic compounds.

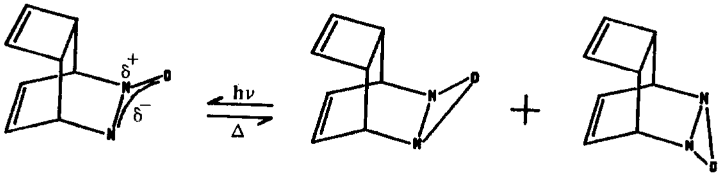


II **I** **III**

Figure 1.

Assignment of the two ODZ isomers is based on the considerable deshielding of the olefinic protons and carbons of **II** relative to **III** (Table 1). An interaction of the π bond with the σ* N-O orbital of the ODZ ring in the exo isomer (Figure 1) would lead to the observed deshielding.[8] Upon warming both isomers are observed to decay back to the original azoxy quantitatively; however, **II** is observed to decay much more rapidly than **III.** This reversion is the first report of differential stability in exo and endo bicyclic ODZ isomers. In agreement with our NMR data the rate difference can be explained by an anchimerically assisted opening of the exo isomer's ODZ ring by the 6,7 double bond (Figure 1).

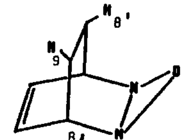
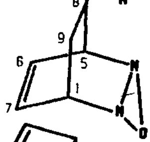
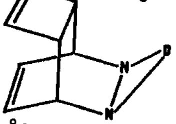
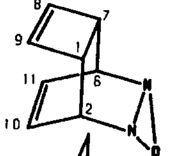
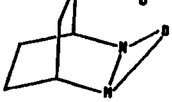
Photolysis of 3,4-diazatricyclo[4.2.2.^{1}0]deca-3,7,9-triene N-oxide (**IV**)^{3} under similar low temperature conditions is also observed to yield a photoequilibrium involving two isomers which can be assigned, from low temperature NMR data (Table 1), as the exo (**V**) and endo (**VI**) ODZ isomers.



IV **V** **VI**

As in the previous case, both ODZ isomers, **V** and **VI** , thermally decay quantitatively back to the original azoxy compounds. Anchimeric assistance is again implicated by the more facile ODZ ring opening of the exo isomer, **V.**

Table 1. NMR Shifts of Oxadiaziridines at -70^{o}C in CD_2Cl_2^{9}

		Protons	δ (ppm)	Carbons	δ (ppm)
	II	$H_{8',9'}$ $H_{8,9}$ $H_{1,5}$ $H_{6,7}$	0.96 1.87 4.47 6.60	$C_{8,9}$ $C_{1,5}$ $C_{6,7}$	22.9 57.6 133.5
	III	$H_{8',9'}$ $H_{8,9}$ $H_{1,5}$ $H_{6,7}$	1.28 1.70 4.36 6.51	$C_{8,9}$ $C_{1,5}$ $C_{6,7}$	17.7 56.6 122.5
	V	$H_{1,7}$ $H_{2,6}$ $H_{8,9}$ $H_{10,11}$	3.06 4.71 5.53 6.33	$C_{1,7}$ $C_{2,6}$ $C_{8,9}$ $C_{10,11}$	37.4 62.1 119.4 137.6
	VI	$H_{1,7}$ $H_{2,6}$ $H_{8,9}$ $H_{10,11}$	3.02 4.53 5.56 5.83	$C_{1,7}$ $C_{2,6}$ $C_{8,9}$ $C_{10,11}$	38.1 61.8 130.5 135.4
	VII	$H_{6,7}$ $H_{8,9}$ $H_{1,5}$	1.27 1.69 3.57	$C_{6,7}$ $C_{8,9}$ $C_{1,5}$	20.2 21.8 53.5

In CD_2Cl_2, we obtain an endo-exo $\Delta G^{\ddagger}$ difference of 2.8 kcal/mol for ring openings of **II** and **III** , and 1.5 kcal/mol for **V** and **VI** (Table 2). Anchimeric assistance in the solvolysis of norbornenyl systems has been extensively studied.

In the original study by Roberts on exo and endo-2-norborn-5-enyl halides, $\Delta G^{\ddagger}$ differences on the order of 1.0 kcal/mol were found.[1] For the analogous tosylate system, $\Delta G^{\ddagger}$ differences on the order of 4.5 kcal/mol have been measured.[10] Brown[11] has ascertained that two factors determine the rates of solvolysis in endo–exo norbornenyl systems; these factors are anchimeric assistance from the π bond, and steric retardation of endo isomers to solvolysis. Our ODZ compounds represent an interesting class in that steric retardation in the endo isomer should not be significant, as the route to the azoxy product entails movement of the oxygen out and away from the π cloud of the 6,7 double bond (Figure 1).

Table 2. ΔG of Activation Values (kcal/mole)[12]

ODZ		CD_2Cl_2	CD_3OD
II	(exo)	16.3	16.8
III	(endo)	19.1	19.2
V	(exo)	16.5	17.2
VI	(endo)	18.0	18.4
VII		18.6	18.3

Brown also shows that the inductive effect of the homoallylic π bond will retard the rate of solvolysis of both endo and exo norbornenyl isomers relative to the saturated norbornyl analogs. Since no formally charged species are involved in our system where a neutral ODZ species produces a neutral azoxy species, this effect would be expected to be minor. In fact ODZ ring opening in the endo isomer **III** has a rate very close to that of its saturated analog (**VII**).[3] A $\Delta G^{\ddagger}$ for **VII** was measured in methanol and found to be 18.3 kcal/mol which is in good agreement with the value previously reported.[7] In addition, the significant difference in rates of ring openings of the exo isomer **II** and the saturated analog **VII** shows that a steric repulsion of the ethane bridge hydrogens and the ring oxygen is not important in the rate acceleration seen with the exo isomer. Thus the rate enhancement of the exo isomer is a true measure of the anchimeric assistance in this system since the effects of steric hindrance and double bond induction are minimal. The approximately 2 kcal/mol difference is then a reflection of the weakening of the N–O bond via the $\pi - \sigma^*$ two electron interaction.[13] This interaction may be stronger than in the norbornenyl tosylate system since the energy of the σ^* orbital will be substantially lower for an N–O bond compared to a C–O bond.[13]

All ODZ ring openings were measured in fully deuterated methylene chloride and methanol. In both solvents, the rate difference for ring opening between **V** and **VI** is smaller than that seen for **II** and **III**. This smaller difference may be due to an interaction between the σ^* N–O orbital and the σ orbital of the cyclobutene ring in the endo isomer, **VI** , thereby weakening the ODZ ring.

For the most part, the relative rates of ring opening increased slightly from CD_2Cl_2 to CD_3OD suggesting that the transition state is less polar than the ODZs. This trend has also been observed for monocyclic ODZ systems.[14] Intuitively, this result seems to be the reverse of what would be expected since a 1,3-dipole is being formed. However in the ODZ moiety the nitrogens have a partial positive charge, while the terminal nitrogen of the azoxy functionality has a partial negative charge.[15] Thus, polarity on this nitrogen center decreases in the transition state which may explain the solvent trend.

Low temperature photolysis of cyclic azoxy compounds and NMR examination of the resulting ODZ isomers has given us insight into the nature of the ODZ → azoxy transition state. These results show that a homoallylic π bond lowers the activation energy of the exo ODZ ring opening by approximately 2 kcal/mol relative to the endo. This work represents a rare example of a nonsolvolytic reaction displaying anchimeric assistance.[16] Furthermore, this assistance may represent true π bond acceleration free of other contributing factors which would be present in solvolysis reactions as discussed for norbornenyl systems.

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(4) Continued photolysis produced dienes and their expected photoproducts in all cases.

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(8) Basis for changes in ^{13}C chemical shifts is not fully understood, but orbital interactions do play a significant role. See Lambert, J. B.; Vagenas, A. R. *Org. Mag. Reson.* **1981,** *17*, 270-277.

(9) Spectra were obtained on a Bruker AM 400 MHz NMR spectrometer. Chemical shifts are referenced to the CD_2Cl_2 resonances at δ 5.32 ppm for ^{1}H and δ 53.8 ppm for ^{13}C. The reported ODZ shifts were measured from the center of each multiplet resonance. All ^{1}H shifts were found to be extremely temperature dependent.

(10) (a) Lambert, J. B.; Mark, H. W. *J. Am. Chem. Soc.* **1978,** *99*, 2304-2308. (b) Lambert, J. B.; Mark, H. W. *Tett. Lett.* **1976,** *21*, 1765-1768.

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(12) The reported $\Delta G^{\ddagger}$ values were determined via integration of appropriately unobscured resonances. A least squares fit analysis of *ln* area versus time yielded a temperature dependent rate of decay from which $\Delta G^{\ddagger}$ was obtained.

(13) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Cur. Chem.* **1977,** *70*

(14) (a) Greene, F. D.; Hecht, S. S. *J. Org. Chem.* **1970,** *35*, 2482-2486. (b) Taylor, K. G.; Swigert, J. *J Am. Chem. Soc.* **1971,** *93*, 7337-7338.

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(16) A literature search on the analogous epoxide systems revealed no information about their stabilities.

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