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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths for I and II (9 pages). Ordering information is given on any current masthead page.

Stereospecificity of 1,3-Dipolar Cycloadditions of *p*-Nitrobenzonitrile Oxide to *cis*- and *trans*-Dideuterioethylene†

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The mechanism of 1,3-dipolar cycloadditions has been a topic of lively debate.[2-4] For nitrile oxide cycloadditions, experimental data have been interpreted either as supportive of a concerted mechanism[2,4] or in favor of a stepwise mechanism with diradical intermediates.[3] Theory has compounded, rather than resolved, this problem: ab initio calculations on the reaction of formonitrile oxide with acetylene predict a concerted mechanism at the molecular orbital level[5] but a stepwise mechanism after inclusion of extensive electron correlation.[6] MNDO predicts a stepwise mechanism with a diradical intermediate.[7] We have studied the stereospecificity of the cycloadditions of *p*-nitrobenzonitrile oxide (**1**, Ar = *p*-NO_2Ph) to *cis*- and *trans*-1,2-dideuterioethylene and have obtained evidence that narrowly circumscribes the mechanism of this typical 1,3-dipolar cycloaddition.

The stereospecificity observed in many 1,3-dipolar cycloadditions[8] is often considered to be compelling, if not conclusive, evidence for concert in these reactions.[2] However, if the rate constant for rotation (k_r) about bond **a** (Figure 1) in a diradical intermediate, **3a** or **3b**, were much smaller than the rate constant for cyclization (k_c), high stereospecificity would still be observed.[3] The reported examples of stereospecific 1,3-dipolar cycloadditions involve di-, tri-, or tetrasubstituted alkenes.[8] Barriers to rotation of simple primary, secondary, and tertiary alkyl radicals are only 0–1.2 kcal/mol,[9] but more highly substituted radicals have barriers

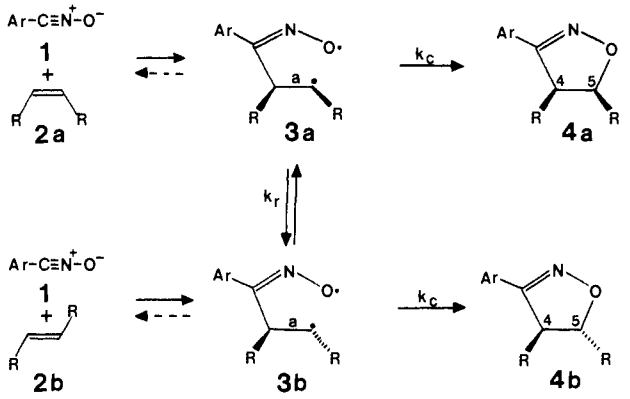

Figure 1. Hypothetical intermediates for stepwise 1,3-dipolar cycloadditions of nitrile oxides to cis- or trans-disubstituted alkenes.

to rotation estimated to be as high as 4 kcal/mol.[10]

Experimental evidence implies that barriers to rotation about single bonds in diradicals are similar to those of analogous monoradicals. For example, while the cupric chloride chlorinations of *cis*- and *trans*-2-butene are largely stereospecific, this reaction is nearly stereorandom with the dideuterioethylenes.[11] Similarly, while rotation is only 0.5–1.4 times the rate of cyclization for 1,2-dimethylbutane-1,4-diyl, rotation is 12 times faster than cyclization for 1,2-dideuterobutane-1,4-diyl.[12] For cycloadditions of tetrafluoroethylene to *trans*-2-butene, 72% of the trans adduct is obtained,[13] while *cis*- and *trans*-dideuterioethylene give the same adduct ratio (probably 1:1) with tetrafluoroethylene.[14] Thus, rotations about single bonds to deuterated primary radical centers in diradicals are very fast relative to cyclization.

If diradical intermediates were formed in the cycloadditions of *p*-nitrobenzonitrile oxide (**1**, Ar = O_2NPh) to *cis*- and *trans*-1,2-dideuterioethylenes (**2**, R = D), then significant scrambling of stereochemistry should be observed in the product. The barrier to rotation of the *n*-propyl radical, a reasonable analogue to **3a** (R = D), is 0.1–0.4 kcal/mol.[9] Even if the barrier to cyclization were only 0.1 kcal/mol, and the barrier to rotation were 0.4 kcal/mol, about 27% of the cis adduct should be formed from the trans reactant, and vice versa.

cis- and *trans*-dideuterioethylene were prepared for these studies by the methods of Nicholas and Carroll.[11] Infrared and mass spectral analyses indicated that the dideuterioethylenes were isomerically pure, but different preparations contained 2–9% of monodeuterated ethylene.[15] The reaction of each dideuterioethylene with *p*-nitrobenzonitrile oxide was carried out in methylene chloride solution at room temperature for 2–6 days under a slight pressure of ethylene-d_2. Evaporation of the solvent and thin layer chromatography gave the deuterated 3-(*p*-nitrophenyl)-2-isoxazolines (**4**, Ar = O_2NPh; R = D), mp 158–159 °C,[16] plus some of the nitrile oxide dimer. The NMR spectrum of the undeuterated adduct is an AA′BB′ multiplet, with the resonances due to the protons at C_4 and C_5 centered at 3.36 and 4.57 ppm, respectively. The couplings, J_{cis} = 11.5, J_{trans} = 8.7, $J_{gem(4,4)}$ = −16.0, and $J_{gem(5,5)}$ = −10.0 Hz, are similar to the

† Dedicated to Professor Rolf Huisgen on the occasion of his 65th birthday.

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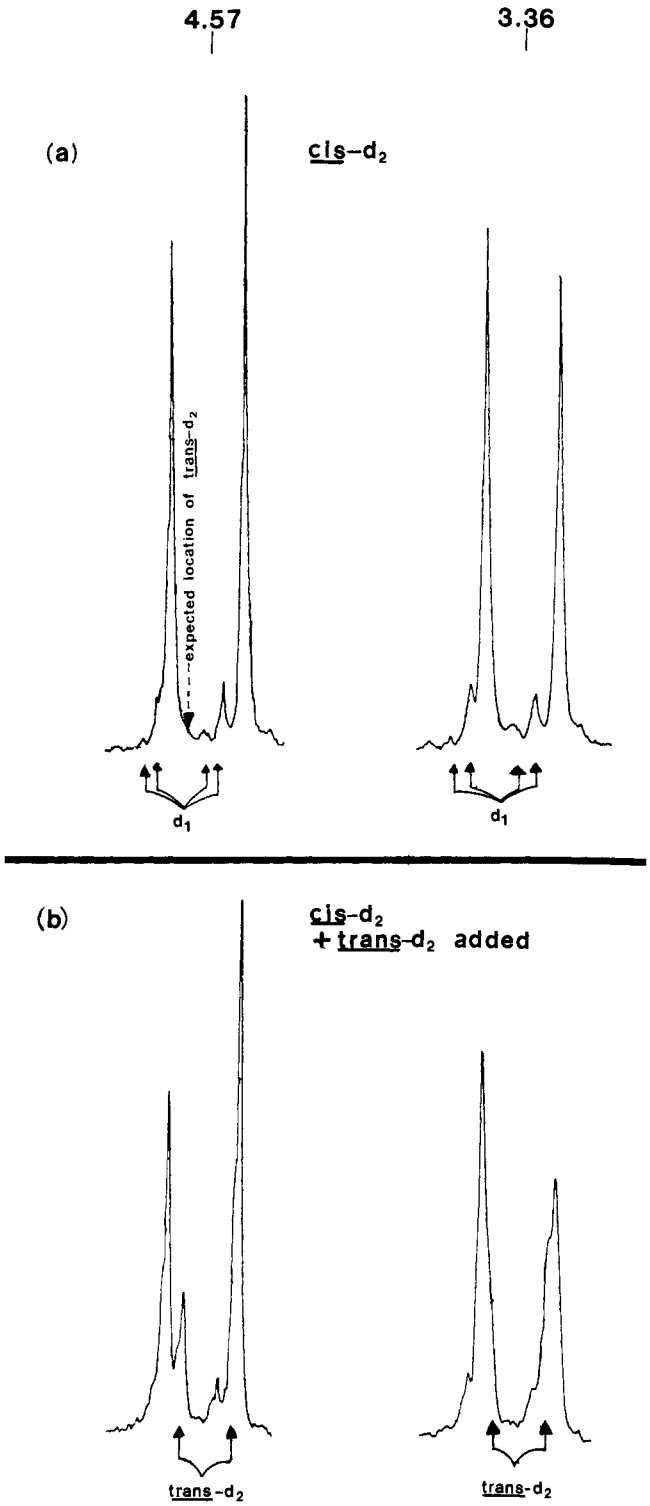

Figure 2. Deuterium-decoupled 200-MHz proton spectra of (a) the *cis*-dideuterioethylene adduct and (b) the cis adduct to which a small amount of the trans adduct has been added.

couplings assigned for the benzonitrile oxide adduct with ethylene.[17] Figure 2a shows the relevant portion of the 200-MHz deuterium-decoupled proton spectrum of the adduct obtained from the reaction of *cis*-dideuterioethylene with *p*-nitrobenzonitrile oxide.

The small impurity peaks are due to the presence of the d_1 adduct, which was prepared from monodeuterioethylene for comparison, and not to the trans-d_2 adduct. The CH_2 resonances of the d_1 adduct appear downfield of CHD resonances of the d_2 adduct, a consequence of a normal upfield shift of proton resonances caused by a vicinal deuterium.[18] Mass spectrometry confirmed that this sample contained 9% d_1. Addition of some of the trans adduct to the cis compound produces the spectrum shown in Figure 2b. This spectrum shows that there is no detectable trans product in the cis adduct. We estimate that as little as 2%, perhaps even 1%, of the trans product could have been detected if it were present in the cis adduct.

These experiments establish that the reaction of **1** with **2** is ≥98% stereospecific. If a diradical intermediate were formed, the barrier to rotation about bond **a** would have to be at least 2.3 kcal/mol higher than the barrier to cyclization. Since the rotational barrier of bond **a** is most likely ≤0.4 kcal/mol, i.e., that expected for a normal primary radical, there can be no barrier to cyclization for the predominant cycloaddition pathway. The most reasonable mechanism for this 1,3-dipolar cycloaddition is the concerted one. Although we have found no evidence for a competing stepwise mechanism, our experiments do not exclude the possibility that a slower stepwise mechanism occurs at a rate that is more than 10 times slower that the rate of the concerted reaction.[19] While these results confirm the concerted mechanism for this 1,3-dipolar cycloaddition, calculations[5] indicate that the concerted transition state is asynchronous, with somewhat more CC than CO bonding in the single transition state separating reactants from products.[20]

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(19) For example, if the stepwise reaction gave only 27% stereochemical crossover, then 2% of the trans adduct would be formed overall from the cis reactant if the concerted reaction were 13 times faster than the stepwise. Competing concerted and stepwise mechanisms have been postulated for various Diels–Alder reactions. See, for example: Bartlett, P. D.; Mallet, J. J.-B. *J. Am. Chem. Soc.* **1976**, *98*, 143 and references therein.

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Ionic Multimers from Heterocyclic Compounds. Clusters or Polymers?

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Recently, we discovered that high-pressure ion/molecule reactions of cyclic oligomers of methylenenitramine ($-CH_2NNO_2-$) and formaldehyde ($-CH_2O-$) give rise to a series of ionic multimers, $[(CH_2NNO_2)_nH]^+$ and $[(CH_2O)_nH]^+$, which can be many times the molecular weight of the oligomeric unit. Our first published report on this subject[1] described ion abundance distributions of two series of ionic multimers $[(CH_2NNO_2)_nH]^+$ generated by ion/molecule reactions of two methylenenitramine oligomers, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) the cyclic trimer, where n = 1–15, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) the cyclic tetramer, where n = 1–56. Enhancements in the ion abundance distributions were observed at n values corresponding to integral molecular units, but some intermediate enhancements also were observed for the HMX

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