absolute stereospecificity when suitable dynamic equilibria cannot be established.

Acknowledgment. We acknowledge the referees who brought Cornforth's discussion of enzyme stereospecificity to our attention and who prompted a more accurate discussion of the consequences of the ordered mechanism. Financial support from the NIGMS (GM-36562) is gratefully acknowledged.

Direct Evidence for Both Thermal and Photochemical Stepwise Cleavage in a Pair of Isomeric Azo Compounds

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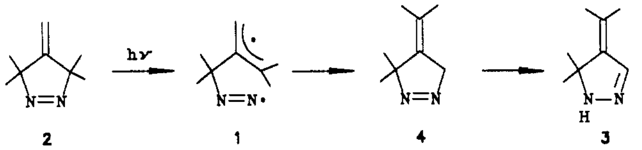
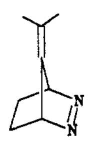
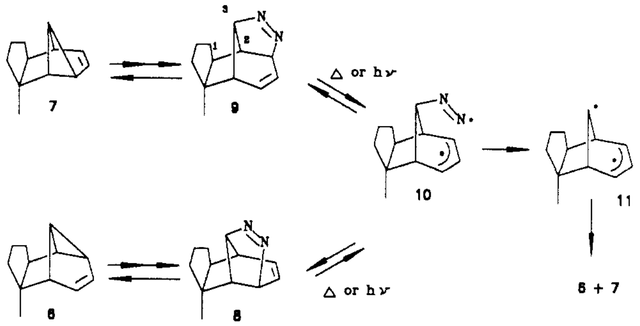
Despite numerous investigations of the formation of biradicals from azo compounds, the question of one-bond versus two-bond cleavage is still poorly resolved.[2] Considerable evidence in favor of initial thermal cleavage of the weakest C–N bond has accumulated.[3-7] Direct support for one-bond cleavage in photolyses of azo compounds is, in contrast, less abundant.[2,8] Recently, Adam and Dörr[9] reported evidence for diazenyl biradical **1** formation in the photochemical denitrogenation of **2**, where 0.5% of rearranged **3** was observed by GC–MS. This product was presumed to be formed from "turnaround" isomer **4**. It was noted that previous efforts by others[10] had failed to detect similar rearrangement in thermolyses of **2**. These results are particularly enigmatic, since similar azo compound **5** is reported to give turnaround thermally but not photochemically.[4b-d] We now wish to report evidence for both thermal and photochemical stepwise cleavage in a pair of isomeric pyrazolines. A theoretical model consistent with known results is proposed.





5

Azo compounds **8** and **9** were synthesized from meta photoadducts of 1-methylcyclopentene and benzene, **6** and **7**, by using procedures detailed by us previously.[11-13] Thermal decomposition of **8** and **9** at 100 °C cleanly gave mixtures of the vinylcyclopropane isomers **6** and **7** in ratios of 2.5:1 and 1:4.9, respectively.



We,[13] and Askani and co-workers,[14] have reported that similar azo compounds exhibit preferential ring closure away from nitrogen and have attributed this selectivity to concerted six-electron cycloreversion. As in our previous studies,[13] the regiospecificity is not complete, and some closure on the same side as nitrogen (e.g., **6** from **9**) is observed. These results suggest that stepwise cleavage of both azo compounds to **10**, and hence to approximately regiorandom product formation (via **11**), occurs in competition with concerted cycloreversion. This scenario raises the possibility of turnaround of the azo isomers, which was confirmed by careful monitoring of the reactions.

HPLC analysis during the thermolysis of **8** showed the formation of a small amount of **9**, which reached a maximum level of 10% of starting **8** and then decreased along with **8**. Similarly, thermolysis of **9** under the same conditions gave production of **8** up to a steady-state concentration of 4% of starting material. Simplex fitting[15] of the concentrations to first-order kinetics indicates that 28% of **8** produces **9** and 13% of **9** gives **8**. High field ^{1}H NMR taken at short thermolysis times confirmed the rearrangement of the isomers. Strikingly, irradiation also caused turnaround of the azo isomers, although to a lesser extent. Photolysis of **8** or **9** at 366 nm produced a maximum level of ca. 2% (based on the amount of starting azo compound) of the alternate azo isomer, along with **6** and **7**. The azo compounds have comparable absorptions at this wavelength.[11]

These results suggest at least some stepwise cleavage in both of these thermal and photochemical denitrogenations. Adam and

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[15] The concentrations of azo compounds relative to an internal standard were fit to an interconverting unimolecular scheme with the SMPLXKS program, from Serena Software, Bloomington, IN. The best-fit rate constants are $k(\mathbf{8},\mathbf{9}) = 5.3 \times 10^{-4}$, $k(\mathbf{8},\mathbf{6}+\mathbf{7}) = 1.36 \times 10^{-3}$, $k(\mathbf{9},\mathbf{8}) = 2.3 \times 10^{-4}$, and $k(\mathbf{9},\mathbf{6}+\mathbf{7}) = 1.69 \times 10^{-3}\ \mathrm{s}^{-1}$ at 99.4 °C. It should be noted that the regiochemistry of product formation is too random to be accounted for by rapid equilibration of the azo isomers with selective formation of only **6** from **8** and **7** from **9**. Previous azo compounds of this general structure reported from these laboratories[13] exhibit no turnaround. These compounds were methyl substituted at the 3-position (numbered as in **9**), and the corresponding tertiary diazenyl radicals are likely too unstable to rearrange.[4a,6a,b]

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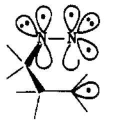
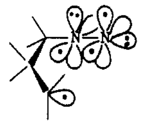
co-workers[3d,9,16] have postulated, based on theoretical work of others,[17] that thermolyses of azo compounds should give ground state σ diazenyl radicals (crudely represented by **12**), whereas photochemical cleavage should initially produce excited-state π-type (e.g., **13**). This proposition follows from Salem diagram symmetry analysis. They argue[9] that direct loss of nitrogen from **12** would produce ground-state nitrogen, but cleavage of excited **13** would give n,π^* N_2. It was suggested that **13** should thus be longer lived than the thermally generated radical, leading to the question why turnaround is not more often observed in photochemical denitrogenations, even in systems giving thermal turnaround (e.g., **5**).

We wish to point out a possible resolution of this dilemma, consistent with larger extents of thermal than photochemical turnaround.[18] This analysis parallels the well-understood behavior of the isoelectronic formyl radical,[19] and similar reasoning has been used to analyze the photochemical α cleavage of cyclic ketones.[20] It should first be noted that significant barriers are predicted for the loss of N_2 from the thermally produced ground-state radical **12**, due to mixing of the σ and π states.[6a,b,21]



12



13

As pointed out by several authors,[17,21] the equilibrium geometry of the excited-state n,π^* diazenyl radical **13** is expected to be linear, as is the isoelectronic excited $HCO^\bullet$ radical.[19] The photochemically formed **13** is, to first order, degenerate with the ground-state σ radical inversional transition state. This surface touching offers an efficient radiationless decay path to the ground-state radical.[19,21] There is hence no reason to expect a photochemically generated diazenyl radical to have a longer lifetime than one formed thermally. In fact, crossing from the excited to the ground electronic surface should produce vibrationally excited diazenyl radical, denitrogenating more readily than the thermally produced intermediate and giving less turnaround. This process is analogous to the known electronic predissociation of excited formyl.[19] Hot diazenyl radicals might also explain the photochemical formation of biradicals from azo compounds at low temperatures, under conditions where diazenyl radicals are expected to be stable.[22]

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Supplementary Material Available: Spectral data and select synthetic details for new compounds **6–9** and the precursor urazoles (3 pages). Ordering information is given on any current masthead page.

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Singlet Oxygen Production from the Reaction of Superoxide Ion with Halocarbons in Acetonitrile

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There is controversy about the mechanism of singlet oxygen ($^1O_2$) formation from systems that contain superoxide ion ($O_2^{\bullet -}$), halocarbons, and H_2O.[1-4] Khan[1] and Corey et al.[2] have proposed that the $^1O_2$ results from the water-induced disproportionation of $O_2^{\bullet -}$, while Arudi et al.[3] and Kanofsky[4] have proposed that the $^1O_2$ is a product of the reaction of $O_2^{\bullet -}$ with halocarbons, where X is Br or Cl. Several prior studies support the latter hypothesis.[5]

$$2O_2^{\bullet -} + H_2O \rightarrow O_2(^1\Delta_g) + HO_2^- + OH^- \qquad (1)$$

$$O_2^{\bullet -} + RX \rightarrow RO_2^\bullet + X^- \qquad (2)$$

$$2RO_2^\bullet \rightarrow [ROOOOR] \rightarrow O_2(^1\Delta_g) + \text{products} \qquad (3)$$

The interpretation of past experimental results is difficult, however, because all prior chemiluminescence studies that demonstrate $^1O_2$ production have used either a two-phase system (halocarbon–^2H_2O/solid KO_2)[4] or a three-phase system (halocarbon/H_2O/solid KO_2).[1,2] Via the use of a homogeneous system with acetonitrile as the solvent, we now report that (1) $O_2^{\bullet -}$ reacts with a number of halocarbons to produce $^1O_2$, (2) the addition of ^2H_2O to $O_2^{\bullet -}$ in acetonitrile does not produce $^1O_2$, and (3) the addition of ^2H_2O to halocarbon plus $O_2^{\bullet -}$ reactions does not increase the yield of $^1O_2$.[6]

Figure 1 illustrates the time course of the 1268-nm emission from the reactions of $O_2^{\bullet -}$ with CCl_4, with CBr_4, with α,α,α-trichlorotoluene, and with 1-bromobutane. Spectral analysis of the infrared chemiluminescence in Table I demonstrates an emission peak near 1268-nm for all the systems studied.[7] As shown in Table II, the addition of ^2H_2O to $O_2^{\bullet -}$ in acetonitrile does not produce 1268-nm emission, and the addition of ^2H_2O to the $O_2^{\bullet -}/CCl_4$ reaction does not increase the yield of singlet oxygen.

The failure of ^2H_2O to produce $^1O_2$ from $O_2^{\bullet -}$ or to increase the yield of $^1O_2$ from $O_2^{\bullet -}$/halocarbon reactions is consistent with prior work[4] but in conflict with the conclusions drawn by Corey

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(7) Quantitative estimates of the $^1O_2$ yield from these reactions could not be made because the concentration of $O_2^{\bullet -}$, a potent $^1O_2$ quencher (Guiraud, H. J.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 1984–1986), varied during the course of the reaction.

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