Stereospecific Cycloreversion of an Azoalkane Cation Radical: The Role of the 1,4-Biradical

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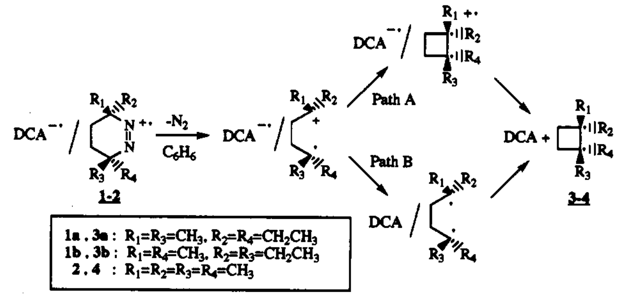
In a classic experiment, Bartlett and Porter showed that the thermal and photochemical decomposition of *meso*- (**1a**) and *d,l*- (**1b**) 3,6-diethyl-3,6-dimethyldiazacyclohex-1-ene was highly stereospecific.[1] They concluded that the rate of ring closure of the putative 1,4-biradical intermediate to yield cyclobutane products was significantly faster than C–C bond rotation. Our interest in azo cation radicals led us to question whether the photo*oxidative* decomposition of **1a,b** would also be highly stereospecific.[2,3] In particular, would the potential 1,4-cation radical intermediate face a fate similar to that of the 1,4-biradical? In this regard, we have found that the reaction is indeed stereospecific; however, our experiments suggest that it is ultimately the 1,4-biradical which determines the stereochemical outcome and not the 1,4-cation radical.

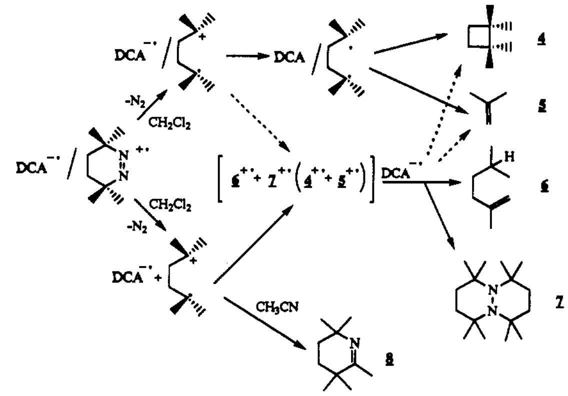
Irradiation ($\lambda > 420$ nm) of dicyanoanthracene (DCA, 0.5 mM) with **1a** or **1b** (7.5 mM) in benzene at 15 °C yields a mixture of *cis*- (**3a**) and *trans*- (**3b**) 1,2-diethyl-1,2-dimethylcyclobutane and 2-methyl-1-butene.[4] The ratio of cis:trans stereoisomers (**3a**:**3b**) from **1a** and **1b** is >20:1 and <1:20, respectively.[4] Photooxidation of 3,3,6,6-tetramethyldiazacyclo-1-hexene (**2**) under similar conditions yields 1,1,2,2-tetramethylcyclobutane (**4**) and 2-methylpropene (**5**). A reasonable mechanism for the cyclobutane formation is shown in Scheme I.

Photoinduced electron transfer from **1** or **2** to the excited state of DCA generates the DCA$^{\bullet-}$/azo$^{\bullet+}$ ion radical pair which subsequently loses nitrogen to yield the 1,4-cation radical.[5] This intermediate can undergo ring closure to the cyclobutane cation radical which is then reduced by DCA$^{\bullet-}$ (Path A). Alternatively, the 1,4-cation radical could be first reduced by DCA$^{\bullet-}$ to the 1,4-biradical, which then stereospecifically closes to the cyclobutane (Path B). These two pathways differ only in the relative rates of ring closure and return electron transfer.

Scheme I



Scheme II



In an effort to distinguish these two mechanistic possibilities, azo **2** was photooxidized in a medium polarity solvent (CH$_2$Cl$_2$) where separation of the DCA$^{\bullet-}$/azo$^{\bullet+}$ ion radical pair may compete with nitrogen loss and the subsequent reactions of the 1,4-cation radical. In Path B, separation would potentially increase the lifetime and perhaps alter the chemical fate of the 1,4-cation radical. Irradiation ($\lambda > 420$ nm) of DCA (0.4 mM) with **2** (10 mM) in CH$_2$Cl$_2$ yields **4** (31%), **5** (28.5%), and two new products, 2,5-dimethyl-1-hexene (**6**, 9%) and a 1:1 adduct of the 1,4-cation radical and azo **2** (**7**, 32%).[4,6] The four products **4**–**7** can all be derived from the 1,4-cation radical, Scheme II. The DCA$^{\bullet-}$/1,4-cation radical pair can undergo electron transfer to the 1,4-biradical and then **4** and **5**, or it could yield **4**–**7** via their respective cation radicals, **4**$^{\bullet+}$–**7**$^{\bullet+}$. Alternatively, separation of the DCA$^{\bullet-}$/azo$^{\bullet+}$ ion radical pair and nitrogen loss can also yield the 1,4-cation radical and products **4**–**7** via their respective cation radicals.

To determine which (if any) of these products are derived from a common intermediate, two experiments were conducted. First, the formation of **6** involves an intramolecular [1,5] hydride or hydrogen atom transfer from one of the methyl groups of the 1,4-cation radical. If isotopic substitution decreases this reaction rate, the yield of **6** and that of products involving a common intermediate would be affected. Photooxidation of perdeuteriomethyl **2**, (**2**-d_{12}) in CH$_2$Cl$_2$ yields **4** (31%), **5** (28%), **6** (<2%), and **7** (41%).[4] Although the yields of **4** and **5** are relatively unaffected by deuterium substitution, the yield of **6** is decreased and that of **7** is increased from **2**-d_{12} relative to **2**. Second, the addition of CH$_3$CN (0.2–3.2 M) to the reaction results in decreased yields of **6** and **7** and increased yields of the cyclic imine **8**, which presumably is formed from the interception of the 1,4-cation radical.[2,7,8] Importantly, the yields of **4** and **5** are

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(1) Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, *90*, 5317.

(2) Zona, T. A.; Goodman, J. L. *Tetrahedron Lett.* **1992**, *33*, 6093.

(3) For previous work on the oxidation of azoalkanes see: (a) Engel, P. S.; Robertson, D. M.; Scholz, J. N.; Shine, H. J. *J. Org. Chem.* **1992**, *57*, 6178 and references therein. (b) Bae, D. H.; Engel, P. S.; Hoque, A.; Keys, D. E.; Lee, W.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* **1985**, *107*, 2561. (c) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* **1987**, *52*, 5015. (d) Mendicino, M. E.; Blackstock, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 713. (e) Adam, W.; Grabowski, S.; Miranda, M. A.; Rubenacker, M. *J. Chem. Soc., Chem. Commun.* **1988**, 142. (f) Adam, W.; Dorr, M. *J. Am. Chem. Soc.* **1987**, *109*, 1570. (g) Shine, H. J.; Bae, D. H.; Hoque, A. K. M. M.; Kajstura, A.; Lee, W. K.; Shaw, R. W.; Soroka, M.; Engel, P. S.; Keys, D. E. *Phosphorus Sulfur* **1985**, *23*, 111. (h) Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007.

(4) Compounds **1a** and **1b** were prepared according to literature procedure.[1] Irradiations were conducted in freeze–pump–thawed sealed tubes. Irradiation ($\lambda > 420$ nm, 8 h) of **2** in the absence of DCA results in minimal decomposition (<2% **4** and **5** formed). Under similar irradition conditions with DCA present, complete decomposition of **2** results. The products were satisfactorily characterized by GC, GC-MS, and ^{1}H NMR. Yields were determined by GC using an internal standard. The ratios of **3a**:**3b** were corrected for reactions using 88% **1a** containing 12% **1b** and 80% **1b** containing 20% **1a**. The yields of 2-methyl-1-butene from **1a** and **1b** are 44 and 38%, and the yields of cyclobutane (**3a** and **3b**) are 51 and 57%, respectively.

(5) (a) The loss of nitrogen presumably occurs by an initial C–N bond cleavage to yield either the diazonium/radical or diazenyl radical/cation intermediate, which then loses nitrogen to form the 1,4-cation radical. Alternatively, this intermediate can be reduced by DCA$^{\bullet-}$ to the diazenyl biradical which loses nitrogen. Although the 1,4-cation radical may not necessarily be formed, the conclusions of the described experiments are unaffected. (b) The radical and cation centers of the 1,4-cation radical may have appreciable interaction to the extent that the species might be considered to be the cyclobutane cation radical **4**$^{\bullet+}$. However, electron transfer to **4**$^{\bullet+}$ from DCA$^{\bullet}$ must yield the 1,4-biradical which can partition between products **4** and **5**. Current experiments are aimed at differentiating the chemistry of the ring-opened and ring-closed forms of the 1,4-cation radical.

(6) In contrast, the direct photochemical decomposition of **2** in CH$_2$Cl$_2$ yields only **4** (38%), **5** (58%), and **6** (3%). In benzene, only **4** and **5** are formed.

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significantly less unaffected by the added CH_3CN.[8] Both the effect of added CH_3CN and the observed product isotope effect imply that **6** and **7** are formed from a common intermediate, which does *not* yield either **4** or **5**.[9]

These experimental observations suggest that **6** and **7** are formed via the ion-separated 1,4-cation radical and **4** and **5** are formed via the ion-paired 1,4-cation radical (and subsequently the 1,4-biradical). Although **4** and **5** could be formed via $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$, it seems unreasonable that the rate of closure or cleavage of the 1,4 cation radical should be dependent on the presence (**4** and **5**) or absence (**6** and **7**) of the counterion $DCA^{\bullet-}$.[5] These results also imply that hydride or hydrogen transfer of the 1,4-cation radical to form **6** occurs faster than ring closure to **4** or cleavage to **5**.[5b]

By analogy to **2**, the stereospecific photooxidative decomposition of **1a,b** to yield cyclobutanes **3a,b** in benzene (and CH_2Cl_2) occurs via the 1,4-biradical (formed from the 1,4 cation radical). This implies that loss of nitrogen, return electron transfer, and ring closure all occur faster than C–C bond rotation after the initial C–N bond scission of the azo cation radical. Although the photooxidative mechanism for formation of the 1,4-biradical from **1** is different than from the thermal and photochemical methods, the chemistry and stereospecificity of the 1,4-biradical are similar. In fact, these experiments provide a rather stringent test to demonstrate the generation of biradical intermediates from azo compounds and potentially other suitable precursors.

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(7) The lifetime of the ion-separated 1,4-cation radical is presumably significantly longer than when ion-paired, and so it is more readily intercepted by CH_3CN at low concentrations. Presumably, at higher [CH_3CN], interception of the ion-paired 1,4-cation radical would occur, decreasing the yields of **4** and **5**.

(8) The respective yields of **4**, **5**, **6**, **7**, and **8** are 30, 29, 9, 33, and 0% at [CH_3CN] = O M; 23, 23, 6, 23, and 23% at [CH_3CN] = 0.2 M; 20, 20, 3, 12, and 46% at [CH_3CN] = 0.9 M. The somewhat reduced yields of **4** and **5** with increasing [CH_3CN] may be due to (i) a change in the efficiency in separation of the ion pair due to increased solvent polarity or (ii) chain propagation by $\mathbf{8}^{\bullet+}$ which would increase the yield of products **6**,**8** relative to products **4**,**5**.[2] Importantly, the effect of added CH_3CN affects the yields of **4**,**5** and **6**,**7** differently.

(9) This effect can be described as an induced kinetic isotope effect. See: Samuelson, A. G.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1981**, 354.