## UV-Laser Photochemistry of the Azoalkane 2,3-Diazabicyclo[2.2.2]oct-2-ene: Trapping of the Short-Lived, Triplet Biradical 1,4-Cyclohexadiyl by Molecular Oxygen

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Trapping of photochemically generated biradicals by molecular oxygen has been demonstrated to serve as an effective and convenient technique for the synthesis of novel peroxides and for the detection and characterization of elusive biradical intermediates. Early examples have been summarized recently,[1] in which the 1,4-preoxetane biradicals derived from the Paterno–Büchi photocyclization of ketones and olefins have been trapped by molecular oxygen to form 1,2,4-trioxanes. More recently the 1,3-biradicals **1a–c** derived from the photolysis of the respective azo compounds
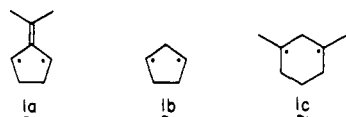
have been trapped with molecular oxygen to form the corresponding bicyclic endoperoxides.[2] It is significant to note that in all of these cases only the triplet states of the 1,3-biradicals were long-lived enough to be trapped by molecular oxygen.

To the best of our knowledge[3] it has not been possible to trap simple, unstabilized triplet 1,4-biradicals such as 1,4-cyclohexadiyl (**2**) to produce the corresponding bicyclic endoperoxide **3** (eq 1).
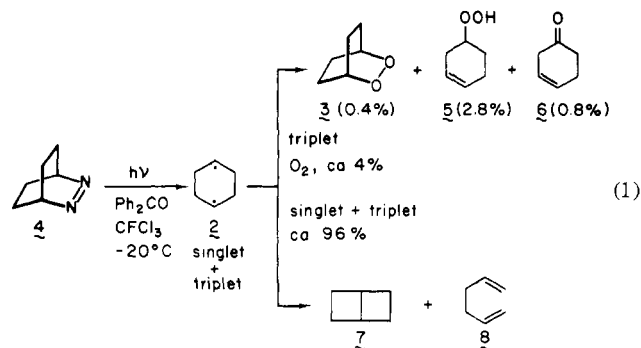
In this report, we describe the results of the oxygen trapping of triplet 1,4-cyclohexadiyl (**2**) generated from the photoextrusion of nitrogen from 2,3-diazabicyclo[2.2.2]oct-2-ene (**4**).[4] Azoalkane

4 constitutes the first of a rather extensive class of photoreluctant azoalkanes to be studied using this oxygen-trapping technique and the results reported here demonstrate that even inaccessible triplet biradicals such as **2** derived from photoreluctant azoalkanes can be trapped successfully and studied by this method.

Due to the low quantum yield for nitrogen loss ($\Phi \sim 1.4\%$) from the triplet state of this photoreluctant azoalkane **4**,[5] it was essential to employ an intense laser source; a Coherent Radiation Model 18 Super Graphite argon ion laser with an output of ca. 3 W in the UV region of interest was used. Adjustment of experimental parameters such as azoalkane concentration, oxygen pressure, and irradiation time was critical in order to obtain optimal results. In a typical experiment, the azoalkane **4** (0.09 M) and benzophenone (0.11 M) in 15 mL of $CFCl_3$ was placed in a Griffin–Worden tube and pressurized to 10 atm with oxygen. After being equilibrated for ca. 1 h, this solution was irradiated with the 363.7-nm line of the laser at –20 °C for 8 h. During this period ca. 65% of the azoalkane **4** had been consumed. Careful removal of the solvent and chromatography on silica gel at –20 °C, eluting with CH_2Cl_2, afforded the mixture of oxygen trapping products **3, 5, 6**, and the mixture of hydrocarbon products **7** and **8** (eq 1).[5] The relative yields in eq 1 were estimated by capillary GLC and ¹H NMR. Traces of 2-cyclohexenone, arising from the facile isomerization of the 3-cyclohexenone (**6**), were detected also.[6]

The structure of endoperoxide **3**[7] was confirmed by comparison of capillary GLC retention times, capillary GLC-MS fragmentation patterns, and 400-MHz ¹H NMR spectra with authentic material. The hydroperoxide **5** was too labile for purification by GLC as it decomposed to a mixture of enone **6** and 3-cyclohexenol.[8] Consequently, $NaBH_4$ reduction of the hydroperoxide sample isolated by chromatography on silica gel afforded 3-cyclohexenol, which was fully characterized by comparison of its MS and ¹H NMR spectral properties with reported values.[9] Due to the ease of isomerization of enone **6** into its conjugated isomer, 2-cyclohexenone, **6** could not be isolated in pure form. However, its MS and ¹H NMR spectral properties[10] were consistent with the proposed structure.[6] Finally, control experiments showed that the oxygen-containing products **3, 5,** and **6** were not derived from the hydrocarbon products **7** and **8**, since the latter were stable under the conditions used in the irradiation of the azoalkane **4**.

It must be emphasized that the azoalkane **4** n,π* transition[11] occurs in the same spectral region as the benzophenone n,π* transition, i.e., 350–400 nm. Thus, it is not possible to excite only the benzophenone sensitizer without populating the singlet excited state of **4** to some extent. It is known further that both the singlet and triplet states of **4** lose nitrogen in temperature-dependent processes which occur with about equal but very low probability (ca. 0.1% at –20 °C).[12] In addition, the singlet state of **4** is exceptionally long-lived (434 ns at 25 °C).[12] In the presence of oxygen (air-saturated solutions), oxygen-induced intersystem crossing of singlet to triplet **4** is thought to proceed quantitatively.[5] Consequently, in this work, the combination of high oxygen pressure and benzophenone sensitization should ensure that singlet **4** is completely converted to triplet **4** and, hence, that the triplet 1,4-biradical **2** is formed quantitatively. If the 1,4-biradical **2** is

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(3) Dervan, P. B.; Dougherty, D. A. In "Diradicals"; Bordon, W. T., Ed.; Wiley-Interscience: New York, 1982. A special case is the 2,3-dimethylene-1,4-cyclohexadiyl biradical; however, this doubly allylically stabilized biradical possesses a relatively long-lived triplet ground state so that oxygen trapping is possible under normal photolysis and even thermal conditions; cf.: Roth, W. R.; Scholz, B. P.; Breuckmann, R.; Jelich, K.; Lennartz, H.-W. *Chem. Ber.* **1982**, *115*, 1934.

(4) (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Adam, W.; De Lucchi, O. *Angew. Chem.* **1980**, *92*, 815.

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(10) MS (70 eV), *m/e* 97 (4%, M + 1), 96 (69%, M), 95 (1%), 81 (5%), 69 (1%), 68 (19%), 67 (22%), 66 (2%), 65 (3%), 63 (1%), 62 (1%), 55 (5%), 54 (100%, M – 42), 53 (23%), 52 (2%), 51 (4%), 50 (3%), 43 (1%), 42 (11%, M –54), 41 (10%); ¹H NMR (CDCl₃, 400 MHz) δ 2.45 (m, 4 H), 2.85 (m, 2 H), 5.75 (m, 1 H), 5.90 (m, 1 H).

(11) Mirbach, M. J.; Liu, K.-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122.

(12) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108.

generated quantitatively in its triplet state, as seems to be the case, a trapping efficiency of only ca. 4% was achieved, and **2** is trapped with very much lower efficiency than triplet 1,3-biradicals.[2] In fact under similar conditions triplet 1,3-cyclopentadiyl (**1b**) is trapped with >99% efficiency.[13]

Theoretical work[14] predicts a triplet ground state for trimethylene 1,3-biradical with its terminal methylene groups in a coplanar conformation. The facts that 1,3-cyclopentadiyl (**1b**) can be detected by ESR spectroscopy[15] and trapped efficiently by triplet oxygen[13] confirm the triplet ground state character and indicate an appreciable lifetime for this species. On the other hand, analogous to the tetramethylene 1,4-biradical for which a singlet ground state with a small singlet-triplet energy gap (ca. 1.6 kcal/mol) has been determined theoretically,[16] we expect the triplet 1,4-cyclohexadiyl (**2**) to be a short-lived species. Consequently, the oxygen-trapping efficiency of ca. 4% for triplet **2** vs. ca. >99% for triplet **1b** nicely corroborates this expectation. On the basis of these results, we estimate[17] lifetimes of ca. 0.1 ns for the triplet 1,4-biradical **2** at −20 °C and ca. 900 ns for the triplet 1,3-biradical **1b** at 7 °C.

Finally, of particular interest is the unusually high proportion of hydroperoxide formation in this system. The hydroperoxide and its decomposition products predominate over the endoperoxide **3** in a ratio of ca. 9:1.[18] It is interesting to note that if the nitrogen extrusion occurs with the more or less concerted breakage of both carbon–nitrogen bonds,[19] the triplet biradical **2** will be born in a boatlike conformation **9** (eq 2). With use of cyclohexane as

(2)
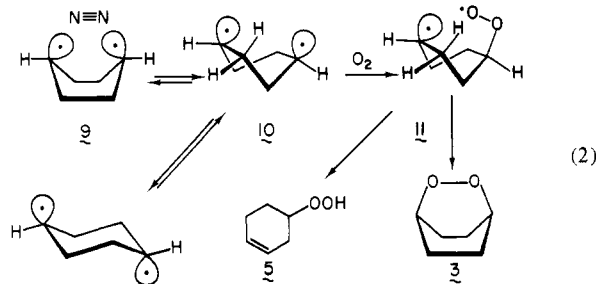
a model, **9** would be expected to immediately relax to a twist-boat conformation **10**, which should be ca. 1.6 kcal/mol more stable than **9**.[20] This twist-boat conformation **10** might be transformed into other members of the twist-boat family of conformers. The lifetime of this initial twist-boat conformer **10** should be ca. 5 × 10^{-10} s at −20 °C, or significantly longer than the lifetime of the biradical itself. In contrast isomerization from the twist-boat manifold of conformers to a chair conformation should have an activation energy of ca. 5.3 kcal/mol.[21] Consequently, the twist-boat family of conformers should have a lifetime of ca. 7 × 10^{-9} s at −20 °C or much longer than that of the triplet biradical species **2**. These considerations indicate that the biradical being trapped has a twist-boat conformation and quite possibly is the initially formed twist-boat conformer **10**. The corresponding conformation of the resulting hydroperoxy biradical **11**[22] has a geometry that should favor hydrogen abstraction to form the hydroperoxide **5** over collapse to the endoperoxide **3** as indicated in eq 2. Related conformational memory effects have been proposed to account for the chemistry of other 1,4-biradicals.[23]

In conclusion, the oxygen trapping of triplet 1,4-cyclohexadiyl (**2**) establishes this laser photochemical technique as a useful method for the study of previously inaccessible, short-lived biradicals. Furthermore, the characterization of the trapping products provides valuable insight into the chemistry of the intermediary biradicals.

(13) Wilson, R. M.; Adam, W.; Hannemann, K., unpublished results.
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(16) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 5409.
(17) This value has been estimated by using modified Stern–Volmer kinetics in which the bimolecular diffusion-controlled rate constant for the oxygen quenching of the biradical was taken to be $k = 2.4 \times 10^9$ M^{-1} s^{-1} (personal communication of J. Wirz, to whom we are most grateful for providing us with this value) and an experimentally determined value for the oxygen concentration in CFCl$_3$ at 10 atm of 0.24 M. In the case of the 1,4-biradical **2**, a lifetime of 7.2×10^{-11} s is obtained if oxygen-catalyzed intersystem crossing is neglected. If one assumes equal contributions to biradical quenching from trapping and catalyzed intersystem crossing, a lifetime of 1.4×10^{-10} s is obtained. In the case of the 1,3-biradical **1b**, it is known that oxygen-catalyzed intersystem crossing is negligible, since virtually all hydrocarbon formation is suppressed (<1% hydrocarbon formation) at oxygen pressures greater than about 2 atm. At this time it is not clear why oxygen-catalyzed intersystem crossing of the simple triplet biradical **1b** does not appear to be an important process. It has been reported to be the major oxygen-quenching route with much more complex, delocalized 1,4-biradicals (Caldwell, R. A.; Creed, D. *J. Phys. Chem.* **1978**, *82*, 2644. Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4512). More quantitative work is being done in an effort to evaluate the factors that influence the partitioning between oxygen-catalyzed intersystem crossing and oxygen trapping.
(18) Since the enone **6** (0.8%) is a secondary product derived from the hydroperoxide **5** (2.8%), the total relative yield of **5** is 3.6% and the ratio of **5**/**3** is 3.6%:0.4%, or about 9:1.
(19) As yet there is no experimental evidence that photochemical nitrogen extrusion from symmetrical azo alkanes such as **4** is a stepwise process. In the case of 1,3-cyclopentadiyl (**1b**), it is known that the species being trapped has lost the nitrogen, as trapping occurs with equal efficiency from both faces of the biradical: Adam, W.; Hannemann, K.; Oppenländer, T., unpublished results.

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(21) Squillacote, M.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1975**, *97*, 3244.
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Conversion of Cyclohexenes into π-Complexed Arenes

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We have had a continuing interest in the reactions of metal atoms with unsaturated substrates to form organometallic species.[1] The conventional route to bis(arene)chromium compounds involves cocondensation of chromium atoms and arenes. This procedure is of little value for the synthesis of chromium π-complexes with nonvolatile ligands which are not amenable to cocondensation reactions. We have sought to develop a new route to bis(arene)chromium(0) compounds by the generation of reactive intermediates that on addition of a suitable arene will yield the desired organometallic complex. Several examples of our proposed strategy which employ iron and nickel atoms have been reported recently.[2–4]

Cocondensation of chromium atoms with 1-butene has been shown by Skell[5] to result in isomerization of the olefin; however,

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