FORMATION OF A 1,2,4-DIOXAZOLIDINE BY ELECTRON-TRANSFER

PHOTOOXYGENATION OF 1-BUTYL-2, 3-DIPHENYLAZIRIDINE

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Summary: Electron-transfer photooxygenation of 1-buty1-2,3-diphenylaziridine with 9,10dicyanoanthracene in oxygen-saturated acetonitrile yields 4-buty1-3,5-dipheny1-1,2,4dioxazolidine. This peroxide is surprisingly stable in nonpolar solvents decomposing to benzaldehyde and N-buty1benzamide upon heating to 100°C in benzene. Treatment with tripheny1 phosphine yields benzaldehyde and N-buty1-1-pheny1methanimine.

A variety of organic substrates undergo electron-transfer photooxygenation in polar solvents in the presence of cyano-substituted aromatic hydrocarbons such as 9,10-dicyano-anthracene (DCA).¹ The key step in this reaction involves electron-transfer fluorescence quenching of the sensitizer by the substrate. DCA-sensitized photooxygenations have, therefore, been limited to easily oxidized substrates with oxidation potentials of less than 2V vs. SCE in MeCN.^{1b} We have, however, recently described a method by which a compound that does not quench DCA may nevertheless be rapidly oxidized.² For example, photooxygenation of phenyl-substituted oxiranes to yield the corresponding ozonides can be effected by use of biphenyl as a non-light-absorbing cosensitizer in conjunction with DCA.³

Our results on the photochemical conversion of epoxides to ozonides have led us to investigate the DCA-sensitized reaction of other heterocycles. We now provide the first report of the electron-transfer photooxygenation of an aziridine and the isolation of the resulting 1,2,4-dioxazolidine.^{4,5} Photooxygenation of cis-1-n-butyl-2,3-diphenylaziridine (1)⁷ was



carried out in dry MeCN with $1 \ge 10^{-2}$ M <u>1</u> and $2 \ge 10^{-4}$ M DCA. The solution was irradiated at 10°C under oxygen with a 450-W medium-pressure mercury lamp using a CuSO₄-filter solution.⁸ The reaction was complete in 1.5 h as determined by reverse phase HPLC. The addition of biphenyl as a cosensitizer was not necessary in this case as aziridine <u>1</u> efficiently quenches the fluorescence of DCA in MeCN (k_q = 8.2 $\ge 10^9$ M⁻¹ s⁻¹, E^{OX}_p = 1.7 V vs. SCE in MeCN). Removal of the solvent under vacuum and analysis of the products in CDCl₃ by 300 MHz ¹H NMR indicated the formation of 83% of 4 - <u>n</u>-butyl - 3,5-diphenyl-1,2,4-dioxazolidine (<u>2</u>) along with benzaldehyde (<u>3</u>). Peroxide <u>2</u> was obtained as a 87:13 mixture of stereoisomers. By analogy to the corresponding phenyl-substituted ozonides, ^{3b,9,10} the major product <u>2a</u> with the higher field absorption (δ 5.543) is tentatively assigned the <u>cis</u>-phenyl configuration. The minor <u>trans</u>isomer <u>2b</u> absorbs at δ 5.879. We have found that the ratio of isomers is independent of reaction time and that peroxides <u>2</u> are not significantly decomposed under the reaction conditions. No isomerization of starting <u>1</u> was detected during photolysis. In addition, aziridine <u>1</u> was not oxidized upon irradiation for 4 h with a 400-W high-pressure sodium lamp in oxygenated MeCN containing Rose Bengal, indicating that <u>1</u> does not react directly with ¹0₉.

Pure dioxazolidine $\underline{2}$ (as a mixture of isomers) was obtained in 25% yield by preparative TLC over silica gel. The chromatography must be carried out rapidly as decomposition of $\underline{2}$ occurs on silica gel. The material was shown to be a peroxide by its positive test with acidic potassium iodide and ferrous ammonium thiocyanate. Treatment of the mixture of $\underline{2a}$ and $\underline{2b}$ in C_6D_6 in an NMR tube with Ph₃P at 100°C for 15 min gave $\underline{3}$ and imine $\underline{4}$ in quantitative yields. $\underline{2}$ is remarkably stable to thermolysis exhibiting only 35% decomposition to $\underline{3}$ and N-butylbenzamide ($\underline{5}$) after heating at 100°C for 6 h in C_6D_6 . Cleavage is more rapid in CDCl₃.



We have reported that cosensitized electron-transfer photooxygenation of <u>cis</u>- and <u>trans</u>diphenyloxirane gives rise exclusively to <u>cis</u>-3,5-diphenyl-1,2,4-trioxolane.^{3b} This striking stereochemical result has led us to propose a mechanism for the photochemical conversion of epoxides to ozonides involving concerted addition of ${}^{1}0_{2}$ as a 1,3-dipolarophile to an intermediate carbonyl ylide. A similar mechanism may be operative in the DCA-sensitized photooxygenation of aziridine <u>1</u> (Scheme 1). Electron-transfer quenching of singlet excited DCA by <u>1</u> would form the open aziridine radical cation with <u>6a</u> predicted to be the most stable isomer. Exothermic electron transfer from 0_2^- to <u>6a</u> and <u>6b</u> could yield ${}^{1}0_2$ and the corresponding azomethine ylides <u>7a</u> and <u>7b</u>. 1,3-Dipolar cycloaddition of ${}^{1}0_2$ to <u>7a</u> and <u>7b</u> would form 1,2,4-dioxazolidines <u>2a</u> and <u>2b</u>, respectively. An alternative mechanism involves back electron transfer from DCA⁻ or 0_2^- to <u>6</u> to form <u>7</u> and DCA or ${}^{3}0_2^-$. Ylides <u>7</u> could subsequently react with ${}^{1}0_2$ generated by energy transfer from singlet and triplet DCA to oxygen. ¹¹ The proposed intermediacy of ylides <u>7</u> in the photooxygenation of aziridine <u>1</u> is consistent with the extensive literature on the trapping of photo- and thermally generated azomethine ylides by dipolarophiles. ¹³ In some cases the ylides have also been detected spectroscopically. ¹⁴

Although the mechanism of this reaction is not fully established and the stereochemical assignments of <u>2a</u> and <u>2b</u> must remain tentative, we have been able to demonstrate the first photochemical conversion of an aziridine to a 1,2,4-dioxazolidine. A full study of the stereochemistry of this reaction with isomeric aziridines is in progress.

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Scheme 1







References and Notes

- (1) (a) D. H. R. Barton, G. Leclerc, P. D. Magnus, and I. D. Menzies, J. Chem. Soc., Chem. Commun., 447 (1972); (b) J. Eriksen, C. S. Foote, and T. L. Parker, J. Am. Chem. Soc., <u>99</u>, 6455 (1977); (c) R. K. Haynes, <u>Aust. J. Chem., 31</u>, 121 (1978); (d) K. A. Brown-Wensley, S. L. Mattes, and S. Farid, J. Am. <u>Chem. Soc.</u>, 100, 4162 (1978); (e) I. Saito, K. Tamoto, and T. Matsuura, <u>Tetrahedron Lett.</u>, 2889 (1979); (f) N. Berenjian, P. deMayo, F. H. Phoenix, and A. C. Weedon, <u>ibid.</u>, 4179 (1979); (g) W. Ando, T. Nagashima, K. Saito, and S. Kohmoto, J. Chem. Soc., <u>Chem. Commun.</u>, 154 (1979); (h) S. L. Mattes and S. Farid, <u>ibid.</u>, 126 (1980); (i) J. Eriksen and C. S. Foote, J. Am. Chem. Soc., <u>102</u>, 6083 (1980); (j) L. T. Spada and C. S. Foote, <u>ibid.</u>, <u>102</u>, 391 (1980); (k) A. P. Schaap, K. A. Zaklika, B. Kaskar, and L. W.-M. Fung, <u>ibid.</u>, <u>102</u>, 389 (1980); (1) S. L. Mattes and S. Farid, <u>ibid.</u>, 104, 1454 (1982); (m) A. P. Schaap, L. Lopez, S. D. Anderson, and S. D. Gagnon, <u>Tetrahedron Lett.</u>, 5493 (1982); (n) W. Ando, Y. Kabe, and T. Takata, <u>J. Am. Chem. Soc.</u>, <u>104</u>, 7314 (1982); (o) S. Futamura, S. Kusunose, H. Ohta, and Y. Kaniya, <u>J. Chem. Soc.</u>, <u>Chem. Commun.</u>, 1223 (1983).
- (2) Presented in part at the IX IUPAC Symposium on Photochemistry, Pau, France, July 26, 1982, Abstr. No. ST 15.
- (3) A. P. Schaap, L. Lopez, and S. D. Gagnon, J. Am. Chem. Soc., 105, 663 (1983); (b) A. P. Schaap, S. Siddiqui, S. D. Gagnon, and L. Lopez, ibid., submitted.
- (4) N-unsubstituted 1,2,4-dioxazolidines can be prepared by the reaction of ketones with H₂O₂ and NH₃: E. G. E. Hawkins, <u>J. Chem. Soc. C</u>, 160 (1971). See also N. Duran, <u>J. Org. Chem.</u>, <u>39</u>, 1791 (1974).
- (5) M. V. George has reported that direct UV irradiation of several aziridines in the presence of oxygen gave rise to products that could be rationalized in terms of 10_2 addition to azomethine ylides and subsequent decomposition of intermediate 1,2,4-dioxazolidines.⁶
- (6) (a) V. Bhat and M. V. George, <u>Tetrahedron Lett.</u>, 4133 (1977); (b) V. Bhat and M. V. George, <u>J. Org. Chem.</u>, 44, 3288 (1979).
- (7) R. N. Loeppky and D. H. Smith, J. Org. Chem., 41, 1578 (1976).
- (8) The 1-cm path-length filter solution was prepared from 27 g of $CuSO_4 \cdot 5 H_2O$, 30 g of NaNO2, and 50 mL of conc. NH₄OH diluted with water to 1000 mL.
- (9) cis- and trans-3,5-Diphenyl-1,2,4-trioxolanes exhibit ¹H NMR absorptions in CDCl₃ for the ring protons at δ 6.331 and 6.360, respectively.^{3b} See also: J. H. Hall, R. Huisgen, C. H. Ross, and W. Scheer, J. Chem. Soc., Chem. Commun., 1188 (1971).
- (10) R. Criegee and H. Korber, Chem. Ber., 104, 1807 (1971).
- (11) Evidence for 1 ₀ generation in DCA-sensitized photooxygenations has been reported.¹²
- (12) (a) J. Santamaria, <u>Tetrahedron Lett.</u>, 4511 (1981); (b) L. E. Manring, C. Gu, and C. S. Foote, <u>J. Phys. Chem.</u>, in press. We thank Professor Foote for a preprint of this paper.
- (13) (a) H. W. Heine and R. E. Peavy, <u>Tetrahedron Lett.</u>, 3213 (1966); (b) R. Huisgen,
 W. Scheer, G. Szeimies, and H. Huber, <u>ibid.</u>, 397 (1966); (c) R. Huisgen and H. Mader,
 Angew. Chem., Int. Ed. Engl., 8, 604 (1969).
- (14) (a). H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, <u>J. Org. Chem.</u>, <u>32</u>, 2708 (1967); (b) A. Padwa and L. Hamilton, <u>J. Heterocycl. Chem.</u>, <u>4</u>,118 (1967); (c) T. DoMinh and A. M. Trozzolo, <u>J. Am. Chem. Soc.</u>, <u>94</u>, 4046 (1972); (d) A. M. Trozzolo, T. M. Leslie, A. S. Sarpotdar, R. D. Small, G. J. Ferraudi, T. DoMinh, and R. L. Hartless, <u>Pure Appl. Chem.</u>, <u>51</u>, 261 (1979) and references therein.

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