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FORMATION OF 1,2,4-DIOXAZOLIDINES BY ELECTRON-TRANSFER PHOTOOXYGENATION OF AZIRIDINES

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Summary: DCA-sensitized photooxygenation of *cis*- and *trans*-2,3-diphenylaziridine in acetonitrile yields exclusively *cis*-3,5-diphenyl-1,2,4-dioxazolidine. Photooxygenation of N-alkyl-substituted 2,3-diphenylaziridines provides both isomers of the peroxide. The *cis*/*trans* ratio of isomers decreases with increasing size of the group on nitrogen. These stereochemical results provide support for a proposed mechanism involving addition of singlet oxygen to intermediate azomethine ylides.

We recently reported that aryl-substituted epoxides can be photochemically converted to ozonides by cosensitized electron-transfer photooxygenation with 9,10-dicyanoanthracene (DCA) and biphenyl.[1,2] These results have led us to investigate the DCA-sensitized photooxygenation of other heterocycles. In an earlier communication, we described the electron-transfer photooxygenation of an aziridine and the isolation of the resulting 1,2,4-dioxazolidine.[5] We have now examined the stereochemistry of this reaction. Of particular interest is the observation that only *cis* 1,2,4-dioxazolidine *3a* is formed from the photooxygenation of *cis*-2,3-diphenylaziridine (*1a*) and *trans*-2,3-diphenylaziridine (*2a*). A similar stereochemical result was obtained in the photooxygenation of *cis*- and *trans*-2,3-diphenyloxirane with exclusive formation of the *cis* ozonide.[1c]

Photooxygenations of the aziridines[6] shown in Table 1 were carried out in dry, oxygen-saturated MeCN with 1 x 10^{-2} M substrate and 6 x 10^{-4} M DCA. The solutions were irradiated at 10°C with a 450-W medium-pressure mercury lamp using a CuSO$_4$-filter solution.[1] Reactions were complete in 1.5 - 2 h as determined by reverse phase HPLC. Unlike the previously studied epoxides, which do not quench the fluorescence of DCA and consequently are unreactive in the absence of biphenyl, the more easily oxidized aziridines efficiently quench ^{1}DCA* and react without the addition of the cosensitizer.[5]

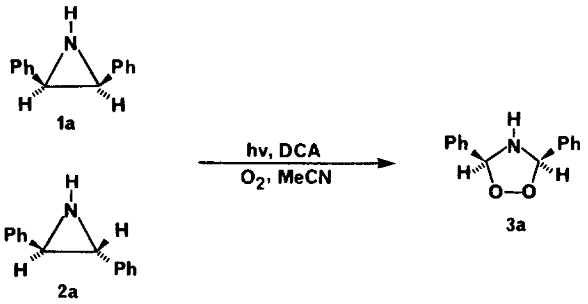
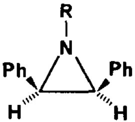
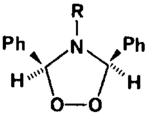
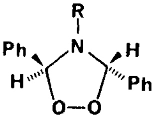
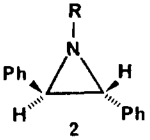
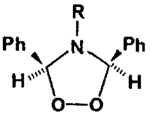
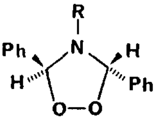


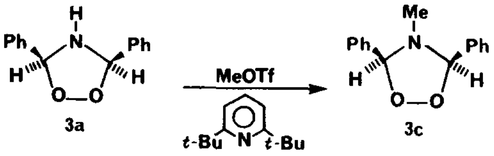
Table 1. Electron-Transfer Photooxygenation of Aziridines.

Aziridine	1,2,4-Dioxazolidines (ratio of isomers)^a			Yield (%)^b	^{1}H NMR for ring protons (δ)	
					cis-3	trans-4
 1	 3		 4			
1a, R = H	100	:	< 1	39	5.937	—
1b, R = Et	87	:	13	40	5.563	5.884
1c, R = Me	85	:	15	40	5.379	5.808
1d, R = n-Bu	87	:	13	83	5.543	5.879
1e, R = $PhCH_2$	40	:	60	40	5.673	5.886
1f, R = t-Bu	< 1	:	100	48	—	5.918
 2	 3		 4			
2a, R = H	100	:	< 1	36		
2b, R = Et	86	:	14	39		

[a] Ratios of 3 and 4 were determined by 300 MHz ^{1}H NMR at partial and full conversion of 1 and 2. [b] Combined yields of both isomers were established by NMR using an internal standard.

The products were analyzed by removal of the solvent at 0°C under vacuum and acquiring 300 MHz ^{1}H NMR spectra in $CDCl_3$. The dioxazolidines were further characterized by reduction with Ph_3P to yield benzaldehyde and the corresponding imines which were compared to authentic samples.[5] In addition to the peroxides, benzaldehyde and n-alkyl-substituted benzamides are products of the photooxygenations.[5] Although the mechanism for the formation of these products has not yet been determined, we have shown that in most cases the dioxazolidines are stable to the reaction conditions. Only the trans peroxides 4e and 4f with large alkyl substituents undergo slow DCA-sensitized decomposition upon extended irradiation. The aziridines do not isomerize during the photooxygenations. In addition, aziridine 1d was not oxidized upon irradiation for 4 h with 400-W high-pressure sodium lamp in oxygenated MeCN containing Rose Bengal, indicating that 1d does not react directly with $^1O_2$.

In our previous report, we indicated that photooxygenation of the n-butyl-substituted aziridine 1d gave an 87:13 mixture of stereoisomers.[5] By analogy to the corresponding phenyl-substituted ozonides,[1c] the major product 3d with the higher field ^{1}H NMR absorption for the ring protons was tentatively assigned the *cis*-phenyl configuration. We have now been able to confirm our original assignment and unambiguously establish the stereochemistry of the dioxazolidines. Photooxygenation of *cis*-1-benzyl-2,3-diphenylaziridine (1e) in MeCN for 30 min gave a combined yield of 40% for the peroxides with an isomeric ratio of 40:60. The minor isomer 3e exhibited two 2H singlets at δ 5.673 and 4.102 while the major isomer 4e exhibited a 2H singlet at δ 5.886 and a 2H AB quartet for the diastereotopic N-benzyl protons at δ 3.700 and 3.779 (J = 13.2 Hz). These results indicate that ring protons for the *cis* dioxazolidines appear at higher field. As only one isomer was observed from the photooxygenation of the N-unsubstituted aziridines 1a and 2a, the chemical shift of the ring protons could not be used to assign the structure of this peroxide. However, treatment of the N-unsubstituted dioxazolidine in $CDCl_3$ with 1.2 equivalents of methyl triflate in the presence of 2,6-di-*t*-butylpyridine afforded in 80% yield the *cis* isomer 3c of the N-methyldioxazolidine.



We have suggested that the stereoselective formation of the *cis* ozonide from *cis* and *trans*-2,3-diphenyloxirane could be rationalized in terms of a mechanism involving concerted addition of $^1O_2$ to an intermediate carbonyl ylide.[1c] A similar mechanism was proposed for the DCA-sensitized photooxygenation of aziridines with addition of $^1O_2$ as a dipolarophile to azomethine ylides (Scheme 1).[5,8] Additional support for this mechanism is now provided by the present stereochemical results. The *cis* dioxazolidine 3a is formed exclusively from 1a and 2a by trapping the more stable ylide 7 (R = H). However, the presence of substituents on nitrogen sterically destabilizes ylide 7 and its radical ion precursor 5 leading to an isomeric mixture of dioxazolidines that is a function of the size of the group on nitrogen.

The proposed intermediacy of carbonyl and azomethine ylides in the electron-transfer photooxygenation of epoxides and aziridines is as yet only a working hypothesis which adequately explains the observed results. This mechanism is, however, in agreement with the extensive literature on the trapping of photolytically and thermally generated ylides by dipolarophiles.[11]

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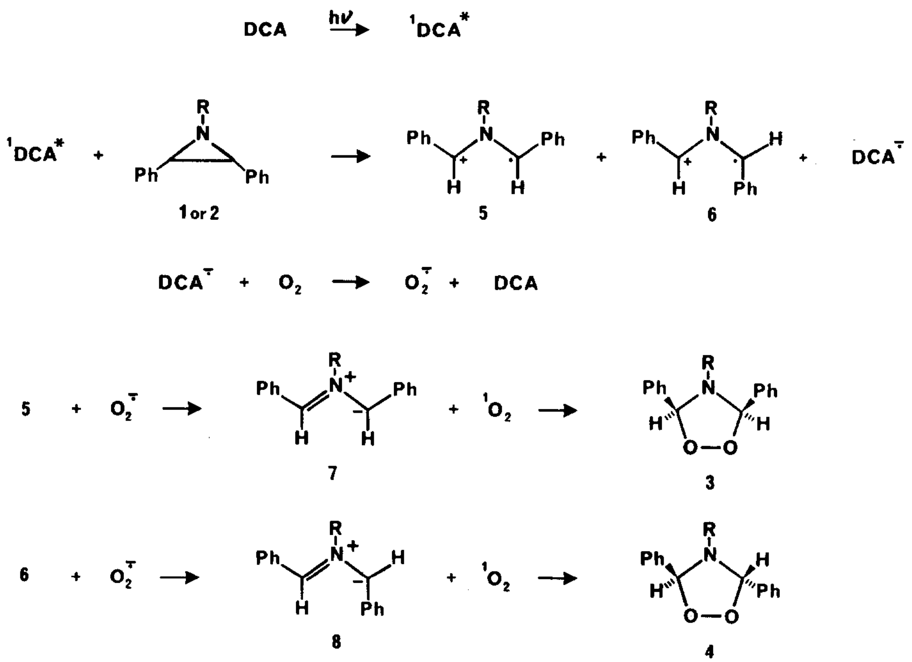
Scheme 1



References and Notes

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2. In related studies, Ohta[3] and Griffin[4] have found that certain epoxides which exhibit low oxidation potentials because of electron-donating groups or ring strain can be oxidized by DCA directly.
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