Stereoselective Formation of Cis Ozonides by Electron-Transfer Photooxygenation of Naphthyl-Substituted Epoxides. Stereochemical Assignments of Ozonides by X-ray Crystallography and Chromatographic Resolution

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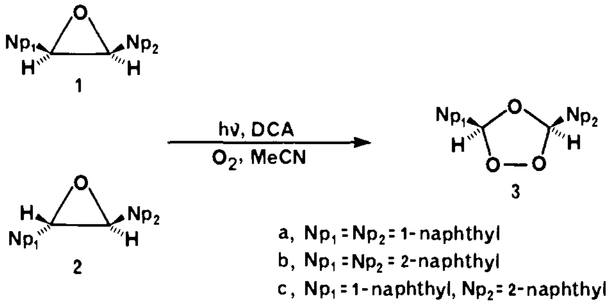
We recently reported that 9,10-dicyanoanthracene (DCA) and biphenyl (BP) can be used to cosensitize the photochemical conversion of aryl-substituted epoxides to the corresponding ozonides.[1] Epoxides which do not quench singlet excited DCA and as a result are unreactive under normal DCA-sensitized conditions may be oxidized in the presence of both DCA and BP. In related studies, Ohta[2] and Griffin[3] have found that certain epoxides that exhibit low oxidation potentials because of electron-donating groups or ring strain can be oxidized by DCA directly.

Insight into the mechanism of DCA–BP-consensitized photooxygenation of epoxides was provided by the observation that only the cis ozonide is formed from *cis*- and *trans*-2,3-diphenyloxirane.[1c] Of concern, however, was the possible influence of the cosensitizer on the stereochemical course of this reaction. We have, therefore, conducted a complementary study of the stereochemistry of DCA-sensitized photooxygenation of more easily oxidized epoxides which do not require the use of BP.[4] We find that cis and trans dinaphthyl-substituted epoxides **1** and **2** also yield exclusively cis ozonides.[7] The stereochemistry of the ozonides has been unequivocally assigned by an X-ray structure of *cis*-3,5-bis(2-naphthyl)-1,2,4-trioxolane (**3b**). The corresponding trans ozonide **4b** was prepared by ozonation of *cis*-1,2-bis(2-naphthyl)ethene and stereochemically identified by chromatographic resolution on a chiral HPLC stationary phase.



(1)

Table I. Properties of Naphthyl-Substituted Ozonides

ozonide	isolated yield from photoox,[a] % (NMR yield)[b]	mp, °C	ring proton ^{1}H NMR, δ[b]
cis **3a**	78 (89)	87–89	7.138
trans **4a**			7.120
cis **3b**	75 (89)	172–174	6.555
trans **4b**		166–168	6.606
cis **3c**	35[c] (80)	108–110	6.614, 7.077

[a] Obtained by photooxygenation of the cis epoxides. Yields from the corresponding trans epoxides were similar. Isolated by preparative TLC and recrystallizated from pentane–CH_2Cl_2 or acetone. [b] NMR spectra were acquired in CD_2Cl_2. Yields were determined by using an internal standard. [c] This ozonide appears to be rather unstable and suffers decomposition during isolation.

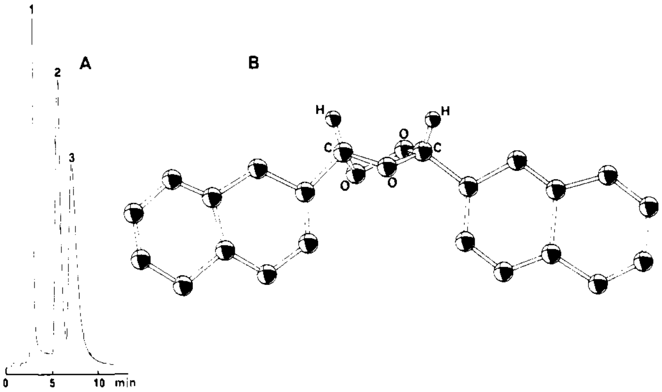


Figure 1. (A) Chromatographic resolution of *trans*-3,5-bis(2-naphthyl)-1,2,4-trioxolane (**4b**) on a μS-Chiralpak OT(+) column (1.5 (i.d.) × 250 mm) and Varian 5000 liquid chromatograph equipped with a UV detector. Flow rate of methanol was 0.2 mL/min. Peak 1 results from a trace impurity of 2-naphthaldehyde; the extinction coefficient 254 nm is much larger for the aldehyde than the ozonides. Peaks 2 and 3 show the separated enantiomers of the trans ozonide. (B) X-ray structure of *cis*-3,5-bis(2-naphthyl)-1,2,4-trioxolane (**3b**).

Photooxygenation of epoxides **1** and **2** was carried out in dry MeCN with 1×10^{-2} M epoxide and 6×10^{-4} M DCA. The solutions were irradiated for 5–15 min at 10 °C under oxygen with a 450-W medium-pressure mercury lamp using a $CuSO_4$-filter solution.[1] Reverse-phase HPLC was used to monitor the reactions. After consumption of the starting epoxide, the solvent was removed at 0 °C under vacuum and the residue analyzed in CD_2Cl_2 by 300-MHz ^{1}H NMR. Spectra exhibited absorptions for only the cis isomers **3** of the ozonides in 80–89% yield (Table I.).[8] The ozonides were further charaterized by reduction with Ph_3P to give 1- or 2-naphthaldehyde. Reactions run to partial conversion show none of the isomeric trans ozonides within the limits of detection by ^{1}H NMR. In addition, no isomerization of the starting epoxides was observed during the photooxygenations.

For comparison, mixtures of cis and trans ozonides were prepared by ozonation of the corresponding alkenes in pentane at low temperature. Treatment of *cis*- and *trans*-1,2-bis(1-naphthyl)ethene with ozone in pentane at −78 °C, removal of the solvent at 0 °C, and analysis in CD_2Cl_2 by NMR indicated a 15% yield of isomeric ozonides in a ratio of 25:75. The minor isomer exhibited the same chemical shift (δ 7.138) for the ring protons as the photo-ozonide **3a** derived from **1a** and **2a**. Ozonation of *cis*-1,2-bis(2-naphthyl)ethene gave a 40:60 mixture of ozonides in 92% yield with the same chemical shift (δ 6.555) for the minor isomer as for the photo-ozonide **3b** derived from **1b** and **2b**. In order to isolate the major isomer (*tran*-3,5-bis(2-naphthyl)-1,2,4-trioxolane (**4b**)), the mixture of ozonides was recrystallized several times from acetone. Examination by NMR of the material

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(2) (a) Futamura, S.: Kusunose, S.; Ohta, M.; Kamiya, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1223. (b) Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Perkin Trans. 1* **1984**, 15.

(3) Kirschenheuter, G. D.; Griffin, G. W. *J. Chem. Soc., Chem. Commun.* **1983**, 596.

(4) (a) Epoxides **1** and **2** exhibit oxidation potentials significantly lower (E_p^{ox} = 1.50–1.59 V vs. SCE in MeCN) than 2,3-diphenyloxiranes and, therefore, quench the fluorescence of DCA with rate constants of (1.37–1.54) $\times 10^{10}$ M^{-1} s^{-1}. Epoxides **1a**, **2a**, **1b**, and **2b** were prepared by literature methods.[5] Oxidation of *cis*- and *trans*-1-(1-naphthyl)-2-(2-naphthyl)ethene[6] by *m*-chloroperbenzoic acid provided epoxides **1c** and **2c**, respectively. **1c**: mp 128–129 °C; ^{1}H NMR ($CDCl_3$) δ 4.734 (1 H, d, 4.4 Hz), 4.881 (1 H, d, 4.4 Hz), 7.200–8.215 (14 H, m); satisfactory analysis. **2c**: mp 101–102 °C; ^{1}H NMR ($CDCl_3$) δ 4.031 (1 H, s), 4.590 (1 H, s), 7.372–8.212 (14 H, m); satisfactory analysis.

(5) Wong, J. P. K.; Fahmi, A. A.; Griffin, G. W.; Bhacca, N. S. *Tetrahedron* **1981**, *37*, 3354.

(6) Everett, J. L.; Kon, G. A. R. *J. Chem. Soc.* **1948**, 1601.

(7) Our stereochemical results stand in contrast to the report by Ohta[2] in which the formation of trans ozonides was suggested.

(8) The remaining material is 1- or 2-naphthaldehyde. The mechanism for the formation of the aldehyde has not been established. However, it is not produced by decomposition of the ozonides under reaction conditions.

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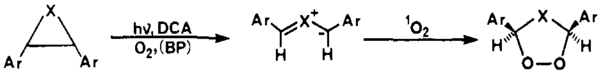
in the mother liquor after the fifth recrystallization showed enrichment (>90%) of **4b** exhibiting an absorption at δ 6.606. This material was further purified by preparative TLC and subsequently recrystallized from acetone to yield pure trans ozonide **4b** (Table I). Ozonation of *cis*- and *trans*-1-(1-naphthyl)-2-(2-naphthyl)ethene in pentane at -40 °C gave a complex mixture of peroxidic products. The NMR spectrum of the mixture showed absorptions for the four ozonides described above as well as absorptions expected for cis and trans ozonides **3c** and **4c**.

In our earlier study of the consensitized photooxygenation of *cis*- and *trans*-2,3-diphenyloxirane,[1c] we had compared the resulting photo-ozonide to authentic cis and trans ozonides prepared by ozonation of stilbene. The stereochemistry of these ozonides had been assigned by Criegee by chromatography over cellulose acetate.[9] The chiral trans ozonide was identified by its partial resolution on this stationary phase.[10] In order to establish the stereochemistry of the naphthyl-substituted ozonides, we have conducted similar experiments utilizing high-performance liquid chromatography over optically active (+)-poly(triphenylmethyl methacrylate).[12] As anticipated, **4b** obtained from ozonation of 2,3-bis(2-naphthyl)ethene was resolved by chromatography over this stationary phase (Figure 1A), confirming the trans dinaphthyl stereochemistry of this ozonide. Chromatography of the photo-ozonides **3a** and **3b** exhibited only one peak consistent with the proposed cis stereochemistry. The structure of ozonide **3b** has also been established by X-ray crystallography (Figure 1B).[13]

The results described herein demonstrate that the same stereochemical course is followed for DCA-sensitized photooxygenation of 2,3-dinaphthyloxiranes as for the DCA–BP-cosensitized reaction with 2,3-diphenyloxiranes. In a related study, we have found that the photooxygenation of *cis*- and *trans*-2,3-diphenylaziridine with DCA yields only the *cis*-1,2,4-dioxazolidine (eq 2).[1c,14b]



(2)

X=O,NH

These stereochemical observations are consistent with a mechanism involving ring-opened radical cation intermediates which may be formed either directly by substrate quenching of ^{1}DCA* or indirectly by electron transfer from the substrate to $BP^{+}\cdot$. As barriers to rotation in these species are quite low,[5,15] equilibration can occur to afford the most stable *E,E* conformation. Back electron transfer from $O_2^{-}\cdot$ or $DCA^{-}\cdot$ to the radical cations would yield the corresponding carbonyl or azomethine ylides (eq 2). Subsequent concerted addition of $^1O_2$ to the ylides would give the observed products. Foote[16] has shown that $^1O_2$ is formed in DCA-sensitized photooxygenations by energy transfer from singlet and triplet excited DCA to oxygen. Singlet oxygen may also be generated as a result of back electron transfer from $O_2^{-}\cdot$ to the radical cation.[17]

Although the proposed intermediacy of ylides in the photoxygenation of epoxides and aziridines is yet to be firmly established, this mechanism is, however, consistent with the extensive literature on trapping of photolytically and thermally genrated ylides.[5,15,18] Experiments are continuing in our laboratory on the mechanism of electron-transfer photooxygenation of epoxides, aziridines, and other substrates.

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Registry No. **1a**, 13528-49-9; **1b**, 81052-73-5; **1c**, 91879-84-4; **2a**, 13528-48-8; **2b**, 81052-72-4; **2c**, 91879-85-5; **3a**, 91879-88-8; **3b**, 91879-86-6; **3c**, 91879-90-2; **4b**, 91879-87-7; **4c**, 91879-89-9; DCA, 1217-45-4; *cis*-1,2-bis(2′-naphthyl)ethene, 2633-08-1; *cis*-1-(1-naphthyl)-2-(2-naphthyl)ethene, 2633-12-7; *trans*-1-(1-naphthyl)-2-(2-naphthyl)ethene, 2633-11-6.

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(9) Criegee, R.; Korber, H. *Chem. Ber.* **1971**, *104*, 1807.

(10) Murray and co-workers had earlier used kinetic resolution by brucine to identify the trans isomer of diisopropyl ozonide.[11]

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(13) Details of the X-ray structure will accompany a full report.

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(17) Santamaria, J. *Tetrahedron Lett.* **1981**, 4511.

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Synthesis and Structure of the First Cyclodiphosphazene. Dimerization of a Phosphonitrile $>P\equiv N$

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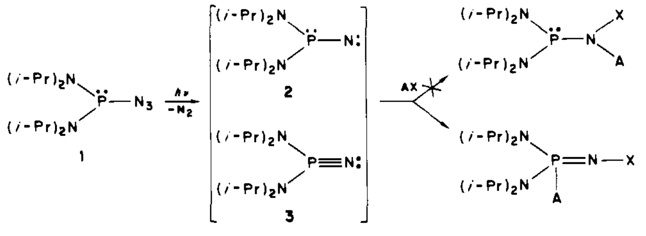
Recently, ab initio calculations have proven that the structure of a singlet phosphinonitrene $>\ddot{P}-\ddot{N}:$ can be formulated to a certain extent as a phosphonitrile $>P\equiv N$, due to delocalization of the lone pairs $n_\pi(P) \rightarrow p_\pi(N)$ and $n_\pi(N) \rightarrow d_\pi(P)$.[1] Indeed, we have shown that the products obtained by photolysis of azidobis(diisopropylamino)phosphine (**1**), in the presence of various trapping agents, could be considered as adducts on a phosphorus–nitrogen triple bond.[2]



AX = MeOH, Me_2NH, Cl–$SiMe_3$,···

Here we wish to report that photolysis of azide **1**, in the absence of any trapping agent, leads to the formation of the phosphonitrile dimer—the first stable cyclodiphosphazene—namely, 2,2,4,4-tetrakis(diisopropylamino)-1,3,2λ^5,4λ^5-diazadiphosphete (**4**). Although several hundred cyclo tri-, tetra-, and polyphosphazenes are known,[3] up to now no examples of cyclodiphosphazenes have

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