# Formation of 1,2,4-Trioxepines *via* 9,10-Dicyanoanthracene(DCA)-sensitized Photo-oxidation of Arylvinyloxiranes[1,2]

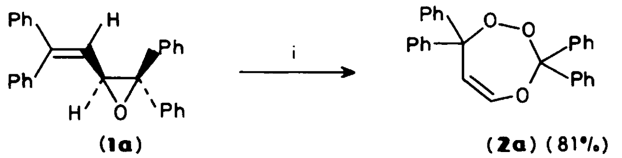
**Shigeru Futamura* and Yoshio Kamiya**

*Department of Reaction Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113 Japan*

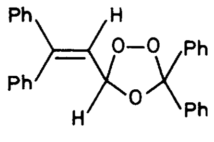
9,10-Dicyanoanthracene-sensitized photo-oxidation of arylvinyloxiranes in acetonitrile affords the corresponding 1,2,4-trioxepines.

Photosensitized electron transfer oxidation of strained molecules is of current interest due to the active oxygen species involved and the potential for the synthesis of cyclic dialkyl peroxides, and various compounds have been oxidized *via* electron transfer mechanisms.[1,3—7]

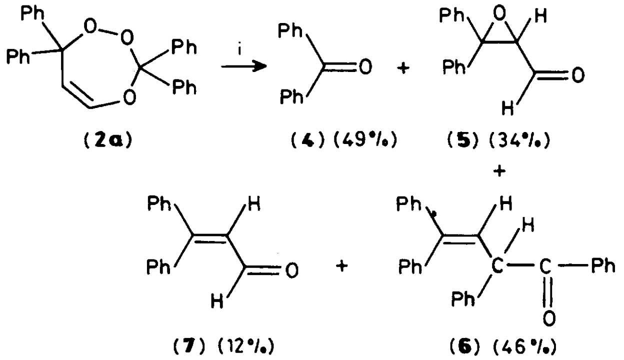
We report here the 9,10-dicyanoanthracene(DCA)-sensitized photo-oxidation of arylvinyloxiranes. 2,2-Diphenyl-3-(2,2-diphenylvinyl)oxirane (**1a**) ($10^{-2}$ mol dm$^{-3}$) was irradiated in acetonitrile through an aqueous 75% $NaNO_2$ solution ($\lambda > 400$ nm) in the presence of DCA ($10^{-4}$



**Scheme 1.** *Reagents and conditions*: i, *hν*/9,10-dicyanoanthracene (DCA)/$O_2$, MeCN, 7 h.



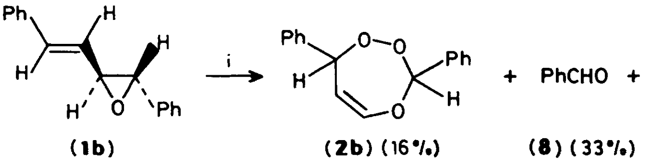
**(3)**



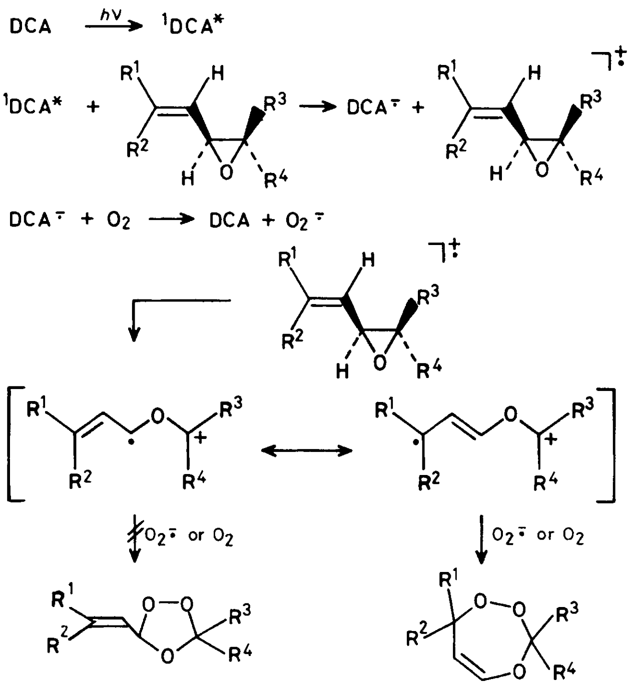
**Scheme 2.** *Conditions*: i, heat.

mol dm$^{-3}$) with $O_2$ bubbling to afford a novel 1,2,4-trioxepine (**2a**), see Scheme 1.

The trioxepine structure could be differentiated from that of 3,3-diphenyl-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (**3**) by monitoring its behaviour toward thermal decomposition and deoxygenation by triphenylphosphine. The thermal decomposition of (**2a**) at 280 °C afforded benzophenone (**4**), 2,2-diphenyl-3-formyloxirane (**5**), phenyl-1,3,3-triphenyl-prop-2-enyl ketone (**6**),† and 3-phenylcinnamaldehyde (**7**) in 49, 34, 46, and 12% yields, respectively, see Scheme 2. It is interesting to note that 3-phenylcinnamic acid, which is a possible decomposition product from (**3**),‡ was not obtained in this reaction. The deoxygenation of (**2a**) by triphenylphosphine in chloroform under nitrogen at room temperature for 12 h afforded (**4**), (**6**), and (**7**) in 47, 46, and 42% yields, respectively. Triphenylphosphine oxide and (**7**) were obtained in stoicheiometric yields. This, and the physical and spectral data§ support (**2a**) as being a 1,2,4-trioxepine.



**Scheme 3.** *Reagents and conditions*: *i*, *hν*/DCA/$O_2$, MeCN, 2 h.



**Scheme 4**

The product distribution is more complicated for the DCA-sensitized photo-oxidation of 2-phenyl-3-styryloxirane (**1b**), see Scheme 3. Trioxepine (**2b**) was isolated only in 16% yield. Neither benzoic acid nor cinnamic acid was obtained in this reaction.¶ Benzaldehyde (**8**), 3,3′-diphenyl-2,2′-bioxirane (**9**), and cinnamaldehyde (**10**) are considered to be derived from the decomposition of (**2b**). The $^1$H n.m.r. and mass spectra of (**9**) were completely superimposable on those of the authentic sample synthesized by another method.

The reaction does not seem to involve singlet oxygen, since (**1**) is stable under the Ru(bpy)$_3^{2+}$-sensitized photo-oxidation conditions. The DCA fluorescence is quenched and linear

---

† *Mass spectral data* for (**6**): *m*/*z* 374 (5.9, *M*$^+$), 269 (100), 191 (75), 105(28), 91 (28).

‡ The independent ozonolysis of 1,1,4,4-tetraphenylbuta-1,3-diene in $CH_2Cl_2$ at −20 °C afforded (**4**) and 3-phenylcinnamic acid in low yields along with tarry materials. Thus, 3-phenylcinnamic acid is considered to be derived from the decomposition of (**3**), by analogy with the thermal decomposition of 3,5-bis(4-methoxyphenyl)-1,2,4-trioxolane affording anisic acid and anisaldehyde in comparable yields.

§ *Physical and spectral data* for (**2a**): m.p. 109.4—110.0 °C, $^1$H n.m.r. ($CDCl_3$) δ, 5.88 (d, 1H, *J* 4.8 Hz), 7.13 (d, 1H, *J* 4.8 Hz), 7.24 (s, 10H), and 7.34 (s, 10H); $\nu_{max.}$ 1635, 1214, 1079, 1053, and 1028 cm$^{-1}$.

¶ 3,5-Diaryl-1,2,4-trioxolanes thermally decompose under the DCA-sensitized photo-oxidation conditions to afford substituted benzoic acids and benzaldehydes.[1]

Stern–Volmer plots are obtained for (**1a**) ($k_q$ = 2.41 × $10^{10}$ $dm^3$ $mol^{-1}$ $s^{-1}$) and (**1b**) ($k_q$ = 1.91 × $10^{10}$ $dm^3$ $mol^{-1}$ $s^{-1}$). In the absence of DCA, (**1**) is stable under the photo-oxidation conditions. It also confirms that DCA, $O_2$, and visible light are all necessary for the reaction.

The addition of 1,2,4-trimethoxybenzene, which has a lower oxidation potential and is unreactive towards DCA-sensitized photo-oxygenation in MeCN,[8] quenches the reaction, indicating that DCA-sensitized photo-oxidation of (**1**) proceeds *via* an electron transfer mechanism. A plausible reaction mechanism is shown in Scheme 4.

S. F. thanks The Kawakami Memorial Foundation for financial support.

*Received, 27th October 1987;*** *Com. 1568*

---

** Received in revised form, 18th April 1988.

## References

1 For Part 3 of the series, 'Photoinduced Electron Transfer Oxidation V,' see S. Futamura, S. Kusunose, H. Ohta, and Y. Kamiya, *J. Chem. Soc., Perkin Trans. 1*, 1984, 15, and references cited therein.

2 For Part 4 of the above series, see S. Futamura and Y. Kamiya, 'The Role of Oxygen in Chemistry and Biochemistry, Proceedings of an International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidations, Studies in Organic Chemistry,' vol. 33, eds. W. Ando and Y. Moro-oka, Elsevier Science Publishers, 1988, Amsterdam, p. 85.

3 K. Mizuno, K. Murakami, N. Kamiyama, and Y. Otsuji, *J. Chem. Soc., Chem. Commun.*, 1983, 462.

4 K. Mizuno, N. Ichinose, and Y. Otsuji, *Chem. Lett.*, 1985, 455.

5 A. P. Schaap, G. Prasad, and S. D. Gagnon, *Tetrahedron Lett.*, 1983, 3047.

6 S. C. Shim and J. S. Song, *J. Org. Chem.*, 1986, **51**, 2817.

7 T. Miyashi, Y. Takahashi, K. Yokogawa, and T. Mukai, *J. Chem. Soc., Chem. Commun.*, 1987, 175.

8 J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083.