Acknowledgment. We thank the National Science Foundation for their generous support of our programs. Drs. N. Cohen and K. K. Chan of Hoffmann-La Roche Co. provided generous comparison samples and Englehardt Industries and Matthey Bishop provided generous gifts of palladium chloride. We are indebted to them.

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(3) For an indirect alternative based upon derivatization, see Valentine, Jr., D.; Chan, K. K.; Scott, G.; Johnson, K. K.; Toth, K.; Saucy, G. *J. Org. Chem.* **1976,** *41*, 62.

(4) While ionization of allylic carboxylates to π-allylpalladium complexes is known, vinyl lactones have been reported only once: Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979,** 2301. For a review see Trost, B. M. *Tetrahedron* **1977,** *33*, 2615.

(5) The vinyl lactones possessing a *Z* olefin were prepared by addition of 1-propynylmagnesium bromide to methyl β-formylpropionate followed by acetylene reduction and methylation. ^{1}H NMR allows assignment of stereochemistry. **6b** vinyl protons: δ 5.74 and 5.49 (J = 10.5; H_a, 2.17; H_b, 2.13; H_R, 2.73; H_c, 5.31 (J_{ab} = 12; $J_{aR'}$ = 8.5; J_{ac} = 5.2, $J_{bR'}$ = ~7.5; J_{bc} = ~7 Hz). **6c** vinyl protons: δ 5.75 and 5.44 (J = 10.5 Hz); H_a, 1.73; H_b, 2.53; H_R, 3.69; H_c, 5.14 (J_{ab} = 12.2; J_{aR} = 10.5; J_{ac} = 10.5; J_{bR} = 5.5; J_{bc} = 8 Hz). Full details will be published in a full account of this work.

(6) All new compounds have been fully characterized including combustion analysis and/or high resolution mass spectra. Known compounds have been fully characterized by spectral means.

(7) In the 270-MHz proton spectrum of **7**a there appeared at δ 1.66 a doublet which may correspond to the methyl group of the allylically transposed product. The signal was <2% of the intensity of the doublet at δ 1.05. Similar doublets in the 270-MHz proton spectra of **7b, 7c, 10a,** and **10b** were <1% of the intensity of the major methyl doublet.

(8) The vinyl lactones possessing an *E* olefin were prepared by addition of 3,3-ethylenedioxypropylmagnesium bromide to crotonaldehyde, hydrolysis, oxidation, and methylation. ^{1}H NMR allows assignment of stereochemistry. 9a vinyl protons: δ 5.82 and 5.56 (J = 16.5 Hz); H_a, 2.22; H_b, 2.07; H_R, 2.69; H_c, 4.92 (J_{ab} = 13; J_{aR} = 8.5; J_{ac} = 4.5; J_{bR} = 8.0, J_{bc} = 8.0 Hz). **9b** vinyl protons: δ 5.49 and 5.84 (J = 16.5 Hz); H_a, 1.62; H_b, 2.53; $H_{R'}$, 2.70; H_c, 4.74 (J_{ab} = 12.2; $J_{aR'}$ = 12; J_{ac} = 10.5; $J_{bR'}$ = 5.5; J_{bc} = 8.2 Hz). Full details will be published in a full account of this work.

(9) Support for this conformation being favored in the ground state arises by the deshielding of H_c in the *Z* olefin isomers **6b** and **6c** relative to the *E* olefin isomers **9a** and **9b** which has been attributed to steric compression. See Cardenas, C. G. *J. Org. Chem.* **1971,** *36*, 1631.

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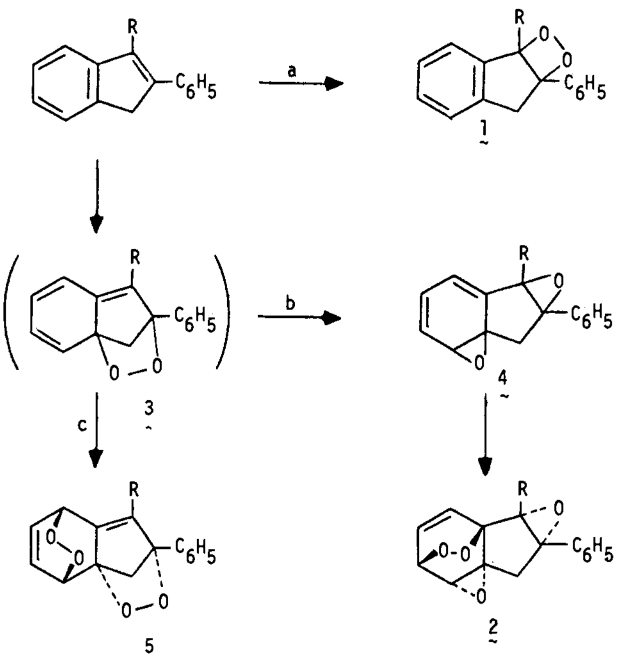
Chemistry of Singlet Oxygen. 32. Unusual Products from Low-Temperature Photooxygenation of Indenes and *trans*-Stilbene[1]

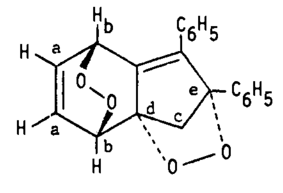
Sir:

Indenes are interesting substrates for photooxidation, producing a wide variety of products. Photooxidation in methanol at −78 °C provides dioxetanes **1** (path a).[2] In acetone at −78 °C (Rose Bengal sensitizer), the observed products are diepoxyendoperoxides **2**.[3] Product **2** is probably derived from a [2 + 4] addition of singlet oxygen to give **3**, followed by rearrangement to a diepoxydiene **4** which is capable of adding a second mole of oxygen (path b). In an effort to learn the origin of this solvent effect, 2,3-diphenylindene was photooxidized at −78 °C in acetone with TPP (*meso*-tetraphenylporphine) as the sensitizer; a novel product was formed (path c).[4,5] The product was stable for extended periods in the solid state, but rapidly decomposed in solution. Explosive decomposition occurred at 110 °C. High resolution mass spectrum was consistent with the molecular formula $C_{21}H_{16}O_4$. The product was assigned structure **5** based on the following data.



R = a: C_6H_5
b: CH_3
c: p-ClC_6H_4

Reaction with triphenylphosphine produced 1.9 equiv of triphenylphosphine oxide, suggesting two peroxide functionalities,[3] and the IR showed no -OH absorption. The ^{1}H NMR (200 MHz) had, in addition to aromatic signals, H_a proton resonances at δ 6.97 (unsymmetrical t)[6a] and 6.81 (unsymmetrical t), H_b protons at δ 5.49 (br d) and 5.28 (br d), and H_c protons as an AB system at δ 3.16 (d, J = 8.5 Hz) and 2.60 (d, J = 8.5 Hz). The ^{13}C NMR (50 MHz) had C_e and C_d resonances at δ 101.2 (s) and 88.9 (s), C_b resonances at δ 72.9 (d) and 71.1 (d), C_c at δ 56.8 (t), and C_a's at δ 133.7 (d) and 130.5 (d), consistent with the assigned structure.[6b] An X-ray crystal structure determination confirmed the structural assignments and showed the stereochemistry of the two oxygen bridges to be anti.[7]



The ratio of the photooxidation products had a strong and unprecedented dependence on the photosensitizer and conditions used. Some conditions produced all three products (**1, 2,** and **5**); however, by careful choice of conditions, any of the three products could be formed preferentially. Table I lists the results with 2,3-diphenylindene using various sensitizers.

The dyes used in runs 5-8 gave ratios of products which changed greatly with only slight changes in the reaction con-

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Table I. Effect of Sensitizer on Product Distribution of 2,3-Diphenylindene

run	solvent	sensitizer	product, % **1a**	**2a**	**5a**
1	acetone	eosin B		88[a]	
2	acetone	RB[b]		93[c,d]	
3	methanol	RB[b]	55[c,e]		
4	acetone	ZnTPP[f]		83[a]	
5	Freon-11	TPP			77[c]
6	acetone	ZnPc[g]	80		20[h]
7	acetone-d_6	MB[i]			100[j]
8	acetone-d_6	HP[k]	5	39	45[l]
9	methanol–acetone (3:7)	TPP	99[a,m]		

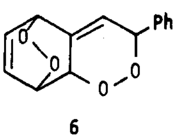
[a] Yield determined by LC. [b] Rose bengal. [c] Isolated yield. [d] Reference 3. [e] Reference 2. [f] Zinc tetraphenylporphine. [g] Zinc phthalocyanine–tetrakis-*N*-alkylsulfonamide. [h] Ratio by NMR. [i] Methylene blue chloride. [j] Only product in NMR. The exact yield was not determined. [k] Hematoporphyrin. [l] Yield by NMR relative to an internal standard. [m] As diketone, after pyrolysis.

ditions. Since the suggested intermediate **3** may either rearrange or add a second $^1O_2$ molecule, conditions leading to a high steady state $^1O_2$ concentration would be expected to trap **3** more effectively and increase the amount of **5** relative to **2**. Thus, high lamp intensity promotes the formation of **5** over **1** and **2**. Similarly, the solvents Freon-11 and acetone-d_6 also favor the formation of **5**. In these solvents, $^1O_2$ has an unusually long lifetime,[8,9] and would thus have a high relative steady-state concentration.

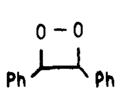
The effect of dye is less certain. One effect would certainly be on the efficiency of light absorption and of $^1O_2$ production; another might be to catalyze the rearrangement of triene endoperoxide **3** to **4**.[10] However, no explanation has yet been developed that is completely satisfactory.

The conditions employed in the preparation of **5a** were applied to the preparation of other diendoperoxides. The following have been isolated (recrystallized yield in parentheses): **5a** (77%), **5b** (82%), and **5c** (62%) from photooxidation in Freon-11, acetone-d_6, and Freon-11, respectively.[5] For comparison, Rose Bengal in acetone at −78 °C gave diepoxyendoperoxides **2a** (93%) and **2b** (78%) as the photooxidation products.[3]

The applicability of these reactions to a nonindene system was tested on *trans*-stilbene. The diendoperoxide was formed in high yield, and an effect of reaction conditions as profound as with the indenes was found. Matsumoto had previously reported the preparation of *trans*-stilbene diendoperoxide (**6**).[4,11]



6



7

Under the reported conditions,[11] at room temperature in CCl_4 using TPP as the sensitizer, the yield of **6** was 16% based on reacted starting material. The other major product, benzaldehyde, was produced in 80% yield. However, at −78 °C in acetone-d_6 using TPP, **6** was produced in 76% yield (by LC analysis). Compound **6** was the *only* product detected in the NMR. Neither benzaldehyde nor its likely precursor, dioxetane **7**,[12] was present. Further, the reaction was much more rapid at −78 °C than at room temperature, as was reported for the indenes.[3] Dye bleaching was a problem, however, with TPP and, to a lesser extent, with Rose Bengal. The analogues of **2** were not formed from stilbene under any conditions investigated. The kinetics and mechanism of these reactions are under current investigation.

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(2) P. A. Burns and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 4339 (1974).
(3) P. A. Burns and C. S. Foote, *J. Org. Chem.*, **41**, 908 (1976); P. A. Burns, C. S. Foote, and S. Mazur, *J. Org. Chem.*, **41**, 899 (1976).
(4) This reaction is similar to the reaction of certain styrene derivatives: (a) M. Matsumoto and K. Kuroda, *Tetrahedron Lett.*, 1607 (1979); (b) D. Lerdal and C. S. Foote, *ibid.*, 3227 (1978); (c) C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, *J. Am. Chem. Soc.*, **95**, 586 (1973).
(5) In a typical preparation, 400 mg of 2,3-diphenylindene was dissolved in 40 mL of Freon-11 containing 4 × 10^{-5} M TPP (saturated). Photooxidation was done at −78 °C in a half-silvered Dewar flask. The light from a 650-W tungsten lamp at 120 V was filtered through a solution of 0.1 g of $K_2Cr_2O_7$ in 50 mL of H_2O (50% cutoff at 510 nm). Oxygen was slowly bubbled into the solution. The reaction was run until complete by TLC (~1 h). Solvent removal gave crystals which were recrystallized from dichloromethane–hexane to yield 77% white microneedles.
(6) (a) The unsymmetrical triplet at δ 6.97 is covered under aromatic signals. However, it could be resolved by decoupling at δ 5.25 and subtracting the decoupled spectrum from the fully coupled. (b) N. R. Easton, Jr., F. A. L. Anet, P. A. Burns, and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 3945 (1974).
(7) C. S. Strouse, J. D. Boyd, L. Goldsmith, and C. S. Foote, unpublished work.
(8) The rate of disappearance of limonene (>510-nm filtered tungsten light, TPP sensitizer) was estimated to be ~14 times greater in acetone-d_6 than in acetone. However, an earlier report gave the $^1O_2$ lifetime in both acetone-d_6 and acetone as 26 μs.[9]
(9) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 7244 (1972); C. A. Long and D. R. Kearns, *ibid.*, **97**, 2018 (1975).
(10) For example, by dye-sensitized rearrangement of **3**, either by energy or electron transfer; the latter mechanism is currently preferred because we have very recently found a very smooth cobalt-catalyzed rearrangement of the same type (J. D. Boyd and C. S. Foote, unpublished work). No evidence for ground-state sensitizer–substrate association has been found.
(11) M. Matsumoto, S. Dobashi, and K. Kondo, *Tetrahedron Lett.*, 2329 (1977); M. Matsumoto, S. Dobashi, and K. Kuroda, *ibid.*, 3361 (1977); M. Matsumoto, S. Dobashi, and K. Kondo, *Bull. Chem. Soc., Jpn.*, **51**, 185 (1978); M. Matsumoto and K. Kondo, *Tetrahedron Lett.*, 3935 (1975).
(12) P. D. Bartlett, M. E. Landis, and M. J. Shapiro, *J. Org. Chem.*, **42**, 1661 (1977).

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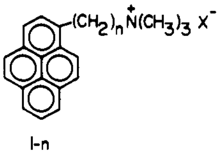
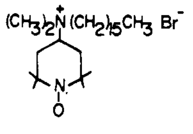
Spectroscopic Studies on Small Aggregates of Amphipathic Molecules in Aqueous Solution

Sir:

Recently we described the fluorescence quenching of several cationic pyrenyl derivatives (**1**-*n* where *n* = methylene chain length) by the surfactant nitroxyl radical **2** (Q) in aqueous solution over a concentration range below and above the critical micelle concentration (cmc = 4.6 × 10^{-4} M) of the latter.[1] At a total quencher concentration of $[Q_T]$ < cmc, there is negligible *diffusional* quenching ($\Phi_0/\Phi \leq 1.1$) of **1**-1 and **1**-5 in contrast to the moderate *static* quenching ($\Phi_0/\Phi \leq 5$) of **1**-11.[2] The latter result shows the tendency of amphipathic materials to associate into premicellar aggregates in aqueous solution. We now report observations on this important, but relatively unexplored, phenomenon using fluorophor **3** (F).



1-n



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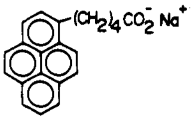

3

Fluorescence Quenching of Sodium 5-(1-Pyrenyl)pentanoate (3). The Stern–Volmer plot of the fluorescence quenching of

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