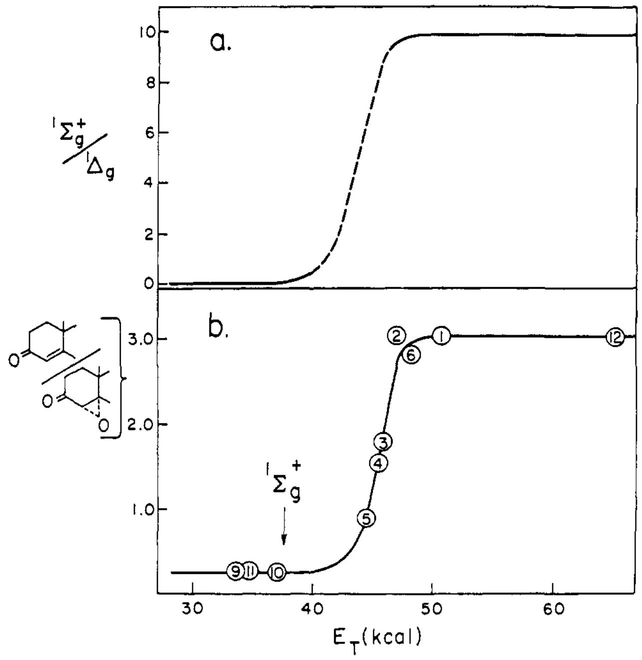

Figure 1. (a) Predicted variation in the $^1\Sigma_g^+:{}^1\Delta_g$ ratio with sensitizer triplet-state energy E_t. (b) Observed variation in the product distribution from the dye-sensitized photooxygenation of cholest-4-en-3β-ol with the triplet-state energy of the sensitizer:[2] (1) fluorescein; (2) eosin Y; (3) sulforhodamin B; (4) erythrosin B; (5) rose bengal; (6) acridine orange; (9) methylene blue; (10) hematoporphyrin; (11) chlorin e_6; and (12) triphenylene.

about 1:4. The dramatic change in the III:II ratio with intermediate energy sensitizers is attributed to the increase in the $^1\Sigma_g^+:{}^1\Delta_g$ ratio as E_t is increased from 38 to 50 kcal. High-energy sensitizers generate mainly $^1\Sigma_g^+$ oxygen, and it appears that this species reacts primarily to give the enone. While the exact nature of the reactivity of $^1\Sigma_g^+$ with I remains to be determined, it is possible that the enone arises from a hydrogen-abstraction-type mechanism involving $^1\Sigma_g^+$.

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Evidence for the Participation of $^1\Sigma_g^+$ and $^1\Delta_g$ Oxygen in Dye-Sensitized Photooxygenation Reactions. II[1]

Sir:

Table I. Product Variation with Concentration of Substrate in the Photosensitized Photooxygenation of Cholest-4-en-3β-ol (I)[a]

Sensitizer	Concn of I[b]	III:II[c]
Methylene blue	1.3×10^{-2}	1:3[d]
	1.0×10^{-4}	1:4–1:5
Fluorescein	1.3×10^{-2}	3:1[e]
	1.0×10^{-4}	1:3
Eosin Y	1.3×10^{-2}	3:1[d]
	8.2×10^{-4}	1:1
	4.0×10^{-4}	1:4
	2.5×10^{-4}	1:4
	1.6×10^{-4}	1:4
	8.2×10^{-5}	1:5
Lumichrome[f]	1.0×10^{-2}	6:1
Riboflavin	1.3×10^{-2}	30:1[d]
	5.0×10^{-4}	6:1
	1.0×10^{-4}	1:2
	7.5×10^{-5}	1:5

[a] The photooxygenation conditions were essentially the same as those used by Nickon,[5] with the exception that a 500-w tungsten lamp was used and typical runs were 24 hr long. [b] Concentration in moles/liter. [c] Ratios determined by chromatography and infrared spectroscopy. [d] This value was also reported by Nickon.[5] [e] Data of Nickon.[5] [f] Irradiation for 3 days.

In the accompanying communication we proposed that both $^1\Sigma_g^+$ and $^1\Delta_g$ singlet oxygen molecules are involved as intermediates in the dye-sensitized photooxygenation of cholest-4-en-3β-ol (I) and that these species exhibit different chemical reactivity toward I.[2] Since $^1\Sigma_g^+$ is known to have a much shorter lifetime in solutions than $^1\Delta_g$,[3,4] a necessary consequence of our "two singlet oxygen hypothesis" is that a reduction in substrate (I) concentration should favor reactions involving $^1\Delta_g$ oxygen. In fact, with sufficiently low concentrations of substrate, only products characteristic of reactions of $^1\Delta_g$ oxygen should be produced (primarily the epoxy ketone II). We examined the effect of cholestenol (I) concentration on the product distribution with five different sensitizers, and the results are presented in Table I. As required by the "two singlet oxygen hypothesis," these data demonstrate the enone: epoxy ketone ratio is very sensitive to the concentration of I when high-energy sensitizers such as fluorescein or eosin are used. A particularly important point is that with sufficiently low acceptor concentrations (10^{-4} *M*) the enone:epoxy ketone ratio is the same as that produced using a low-energy sensitizer, that is, sensitizers which generate only $^1\Delta_g$ oxygen.[2] Furthermore, with the low-energy sensitizer methylene blue, the concentration of I has little effect on the enone:epoxy ketone ratio.

When riboflavin was used as a sensitizer, an unexpectedly high enone:epoxy ketone ratio of 30:1 was obtained.[5] Since riboflavin is known to participate in photoinduced hydrogen-abstraction reactions,[6,7] we were inclined to attribute the large enone production to riboflavin-abstraction reactions rather than to reactions of $^1\Sigma_g^+$ and $^1\Delta_g$ oxygen. We anticipated, therefore, that reduction of substrate (I) concentration would both reduce the importance of direct reaction of riboflavin with I, as compared with energy transfer to oxygen, and favor reactions of $^1\Delta_g$ oxygen over $^1\Sigma_g^+$. We found that with sufficient dilution of enol I (see Table I) we obtained the expected 150-fold decrease in the enone: epoxy ketone ratio from 30:1 to 1:5, the product distribution produced by $^1\Delta_g$ oxygen reactions with I.

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(1) Portions of this work were presented at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 15, 1967. This work was supported by Public Health Service Grant GM-10449, and by the U. S. Army Research Office (Durham) Grant No. G804. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (No. 1956-A1), for partial support of this research.

(2) D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers, and P. Radlick, *J. Am. Chem. Soc.*, **89**, 5455 (1967).

(3) J. S. Arnold, R. J. Browne, and E. A. Ogryzlo, *Photochem. Photobiol.*, 4, 963 (1965).

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Lumichrome is another dye which is structurally similar to riboflavin but has a higher energy triplet state[8] and is a poorer hydrogen abstractor in its excited state than is riboflavin.[9] With lumichrome as the sensitizer and a relatively high concentration of I $(10^{-2}\ M)$, an enone:epoxy ketone ratio of 5.5:1 was obtained. This represents a sixfold change in the product distribution as compared with riboflavin and therefore tends to confirm our interpretation of the riboflavin data and support the "two singlet oxygen" hypothesis.[10]

In view of the demonstrated ability of excited dye molecules to abstract hydrogen atoms from good donors such as phenol,[11] it was possible that enone III production might also be due to hydrogen-atom abstraction by the excited dye molecules. If hydrogen abstraction from I by the excited dye were important in the formation of III, the excited dye would have two competing reaction paths: hydrogen abstraction from I and transfer of energy to oxygen. In this case, the product distribution should be oxygen concentration dependent. This possibility is eliminated with eosin, for example, by the observation that there was no change in the product distribution when the oxygen pressure was varied from 0.2 to 10 atm.[12]

The observed dependence of the enone:epoxy ketone ratio on both the substrate concentration and the sensitizer triplet-state energy is perfectly in accord with the proposed involvement of ${}^1\Sigma_g{}^+$ and ${}^1\Delta_g$ oxygen molecules as intermediates in the sensitized photooxygenation of I. These results do not appear to be consistent with the involvement of some of the other species which have been suggested as intermediates in sensitized photooxygenation reactions.[13,14]

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(8) R. W. Chambers and D. R. Kearns, unpublished results.

(9) B. te Nijenhuis and W. Berends, *Photochem. Photobiol.*, **6**, 491 (1967).

(10) The fact that the enone:epoxy ketone ratio was 5.5:1 rather than 3:1 may possibly be due to a small contribution from hydrogen-abstraction reactions.

(11) L. I. Grossweiner and E. F. Zwicker, *J. Chem. Phys.*, **34**, 1411 (1961).

(12) This conclusion is further supported by the results obtained using triphenylene as the sensitizer.[2] Triphenylene (E_t = 67 kcal) should be much less susceptible to photoreduction than any of the other dyes which were used, and yet when used as a sensitizer it still gave the 3:1 enone:epoxy ketone ratio expected for a high-energy sensitizer.

(13) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).

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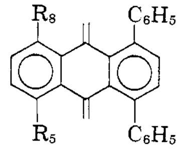
Crowded Anthracenes. I. 1,4,5,8-Tetraphenyl- and 1,4-Diphenyl-9,10-dimethylene-9,10-dihydroanthracene

Sir:

Molecular orbital calculations indicate that quinodimethanes, which lack substituents on the methylene groups, possess unusually high free valence at the terminal carbon atoms.[1] In agreement with these predictions compounds such as *p*-xylylene[2] and 9,10-dimethylene-9,10-dihydroanthracene[3-5] are highly reactive, and ordinary synthetic routes to this type of quinodimethane invariably yield cyclodimer and/or polymer. During a study of the effects of nonbonded aryl groups on the physical and chemical properties of adjacent functionalities we have discovered a set of anthraquinodimethanes that are kinetically stable despite the absence of substituents on the methylene groups. We now wish to report the synthesis of two of these compounds, **1** and **2**.



1, $R_5 = R_8 = C_6H_5$
2, $R_5 = R_8 = H$

Addition of methyllithium to 1,4,5,8-tetraphenylanthraquinone[6] gave the corresponding diol,[7,8] mp 309–312° dec. Treatment of this diol with hydriodic acid in benzene–methanol at 10–30° gave colorless, crystalline **1** in a yield of 80%, $C_{40}H_{28}$, mp 277–278.5° dec, mol wt 489 (isopiestic), and *m/e* 508, $\nu_{\max}^{CS_2}$ 3025, 910 ($C{=}CH_2$), $\lambda_{\max}^{C_6H_{12}}$ mμ (log ε) 229 (4.78) and 273 (4.52), nmr ($CDCl_3$, internal TMS) δ 4.84 (singlet, four methylene protons), δ 7.2–7.6 (multiplet, 24 aromatic protons). Furthermore, both the position and the shape of the peak at δ 4.84 are unchanged over the temperature range of −20 to 200°. The dipole moment of **1**, measured in benzene, amounted to 0.44 ± 0.05 D.

Similarly, addition of methyllithium to 1,4-diphenylanthraquinone[6] gave the diol,[8] mp 167–169°, and treatment with aqueous hydrochloric acid in dioxane gave, after column chromatography, colorless crystalline **2** in a yield of 52%, $C_{28}H_{20}$, mp 162–164° dec, *m/e* 356, $\nu_{\max}^{CS_2}$ 3050, 907 ($C{=}CH_2$), $\lambda_{\max}^{C_6H_{12}}$ mμ (log ε) 223 (4.65), 233 s (4.56), and 273 (4.49), nmr (CCl_4, internal TMS) δ 4.80 (broad singlet, two methylene protons), δ 5.35 (broad singlet, two methylene protons), δ 7.0–7.5 (multiplet, 16 aromatic protons).

The ultraviolet maxima at 273 mμ exhibited by both **1** and **2** are presumably due to the anthraquinodimethane chromophore and are in excellent agreement with the value of 275 mμ predicted by Pullman and coworkers for the unsubstituted hydrocarbon, 9,10-dimethylene-9,10-dihydroanthracene.[9,10]

A nonzero dipole moment for **1** confirms a "boat" or "butterfly" geometry for this quinodimethane and simplifies the interpretation of the nmr spectrum.[11] In this connection a variable-temperature nmr study by Curtin and co-workers has revealed that 10,10-dimethyl-9-methylene-9,10-dihydroanthracene exhibits

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(1) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965, pp 103–120.

(2) The chemistry of *p*-xylylene and its polymers has been reviewed by L. A. Errede and M. Szwarc, *Quart. Rev.* (London), **12**, 301 (1958).

(3) G. Rio, *Ann. Chim.* (Paris), **9**, 229 (1954).

(4) P. Tardieu, *Compt. Rend.*, **248**, 2885 (1959).

(5) J. H. Golden, *J. Chem. Soc.*, 3741 (1961).

(6) E. Bergmann, L. Haskelberg, and F. Bergmann, *J .Org. Chem.*, **7**, 303 (1942).

(7) All new compounds gave satisfactory elemental analyses.

(8) The ultraviolet, infrared, and nmr spectra of this compound are consistent with the assigned structure.

(9) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, E. Fischer, D. Ginsburg, and Y. Hirshberg, *Bull. Soc. Chim. France*, 707 (1951).

(10) This hydrocarbon has been reported by Tardieu[4] to absorb at 283 mμ in ethyl ether at −25°.

(11) Although theoretical treatments assume a planar structure, nothing is known concerning the geometry of the parent hydrocarbon 9,10-dimethylene-9,10-dihydroanthracene.