Polymer-Based Sensitizers for Photooxidations. II[1]

A. Paul Schaap,*[2a] Arthur L. Thayer,[2b]
Erich C. Blossey,[2c] and Douglas C. Neckers[2d]

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received September 6, 1974*

Abstract: The preparation and use of several polymer-bound sensitizers for singlet oxygen generation are described. Photolysis of oxygen-saturated solutions of singlet oxygen acceptors in the presence of the insoluble sensitizer beads provides a convenient method of photooxidation. The quantum yield for the formation of singlet oxygen with polymer-bound Rose Bengal is 0.43. Several synthetic and mechanistic applications of these heterogeneous sensitizers are described.

The reactions of singlet molecular oxygen ($^1O_2$) with various substrates have been under active investigation recently.[3] The intermediacy of singlet oxygen in photosensitized oxidations was originally proposed by Kautsky.[4] This process involves photochemical excitation of the sensitizer to its singlet excited state, intersystem crossing to the triplet state, energy transfer to ground-state oxygen, and subsequent reaction of $^1O_2$ with the acceptor A. Several alternative methods for the generation of singlet oxygen have also been developed: the reaction of sodium hypochlorite with

$$\text{Sens} \xrightarrow{h\nu} {}^1\text{Sens} \qquad (1)$$

$${}^1\text{Sens} \xrightarrow{k_2} {}^3\text{Sens} \qquad (2)$$

$${}^3\text{Sens} + O_2 \xrightarrow{k_3} {}^1O_2 + \text{Sens} \qquad (3)$$

$${}^1O_2 + \text{A} \xrightarrow{k_4} \text{AO}_2 \qquad (4)$$

$${}^1O_2 \xrightarrow{k_5} {}^3O_2 \qquad (5)$$

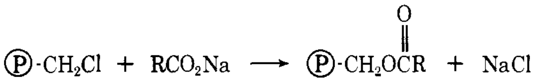
hydrogen peroxide,[5] the thermal decomposition of the ozonides of triphenyl phosphite,[6] 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane,[7] and 2,8,9-trioxa-1-phospha-adamantane,[8] the thermal decomposition of epidioxides,[9] the reaction of potassium superoxide in water,[10] the decomposition of potassium tetraperoxochromate,[11] and the microwave discharge through gaseous oxygen.[12] We recently reported that singlet oxygen is generated by the adrenodoxin reductase-adrenodoxin enzyme system.[13] Other systems thought to produce singlet oxygen include xanthine oxidase,[14] rat liver microsomes, NADPH and O_2,[15] and human polymorphonuclear leukocytes upon phagocytosis.[16]

Although many sources of singlet oxygen are now available, the photosensitized formation of singlet oxygen using various dyestuffs remains the method of choice for most synthetic and mechanistic applications. However, there have been several limitations to the photooxidation method: (1) the sensitizer (dye) must be soluble in the reaction solvent limiting the dye-solvent combinations which can be used; (2) the dye is often bleached over long reaction times; (3) the dye can interact with the substrates and/or the products; and (4) the separation of the dye from the products can be difficult.

In this paper, we describe the preparation of several insoluble polymer-bound dyes and the use of these heterogeneous sensitizers for the photochemical generation of singlet molecular oxygen.[17,18] Polymer-bound sensitizers have several advantages over the free sensitizers in solution. They can be used in solvents in which the unbound dye is both insoluble and therefore unable to sensitize singlet oxygen formation efficiently. They are significantly more stable toward bleaching than are the free sensitizers. The polymer-bound sensitizers can be easily removed at the end of the reaction by filtration, and can be reused with little or no loss in efficiency.

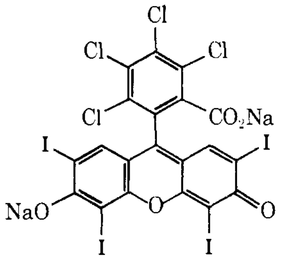
Results and Discussion

The preparation of polymer-bound sensitizers was carried out using experimental procedures developed by Merrifield[19] for polypeptide synthesis. In the Merrifield procedure, chloromethylated styrene-divinylbenzene copolymer beads are converted to carboxylate esters in a nucleophilic displacement reaction (eq 6). The result is a reagent which is placed on a polymer matrix that is compatible with most organic solvents but, by virtue of the polymer structure, is insoluble in them. We have chosen dyestuffs which have been characterized as sensitizers for singlet oxygen formation in solution, and which contained carboxylate groups that could be used for the attachment of the sensitizer to the insoluble polymer beads.



$$Ⓟ\text{-CH}_2\text{Cl} + \text{RCO}_2\text{Na} \longrightarrow Ⓟ\text{-CH}_2\text{O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{R} + \text{NaCl} \qquad (6)$$

Our initial experiments were concerned with the binding of Rose Bengal (1) to the polymer beads and subsequent characterization of this material as an efficient singlet oxygen sensitizer. Rose Bengal contains both carboxylate and phenoxide functional groups, either of which might be capable of reaction with a chloromethyl side chain of the polymer. The dye was attached by heating a Rose Bengal solution in DMF with chloromethylated styrene-divinylbenzene copolymer beads (200–400 mesh, 1.11 mequiv of Cl/g of polymer). Analysis of the resulting polymer-based reagent for its iodine content indicated that one in five chloromethyl residues on the surface of the polymer bead had been converted to the Rose Bengal derivative. The product from this reaction is polymer-attached Rose Bengal, hereafter designated as Ⓟ-Rose Bengal.



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The Ⓟ-Rose Bengal was washed with copious quantities of several solvents to ensure that no free Rose Bengal remained admixed with the polymer. As an additional precautionary measure, the Ⓟ-Rose Bengal was extracted separately with methylene chloride and methanol for several days in a Soxhlet extractor. Therefore, it seems clear that

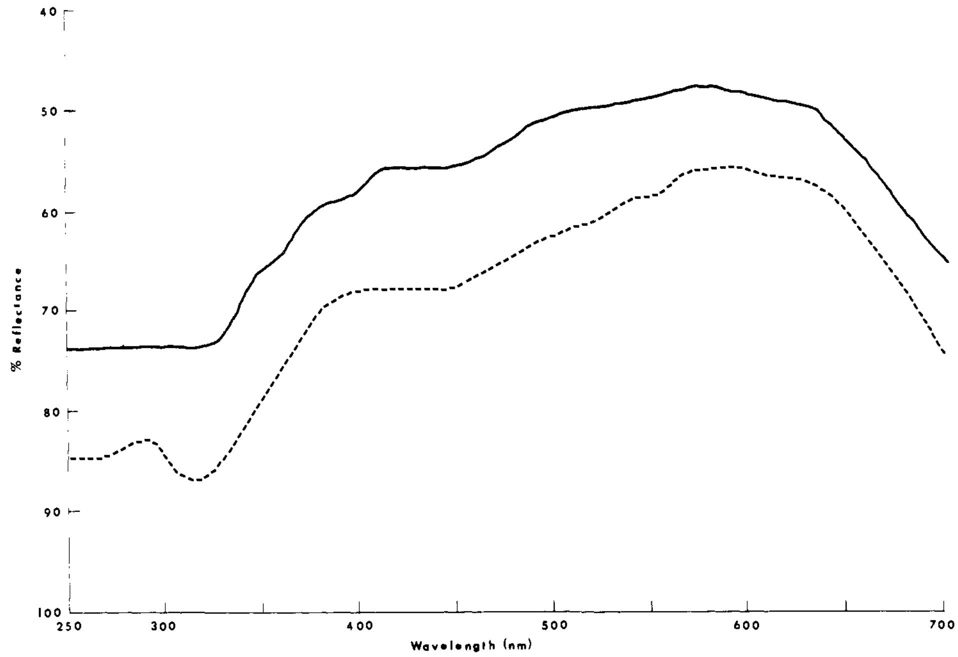
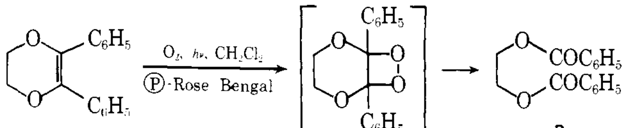


Figure 1. Diffuse reflectance spectra: (—) Rose Bengal in MgO; (- - -) Ⓟ-Rose Bengal in MgO.

the dye is chemically bound to the polymer structure and is not simply trapped in the polymer matrix.

The diffuse reflectance spectrum of Ⓟ-Rose Bengal was compared with that of Rose Bengal in an MgO matrix (Figure 1). The similarity in the diffuse reflectance spectrum of Ⓟ-Rose Bengal and that of free Rose Bengal under similar conditions indicates that the absorption of the polymer-bound sensitizer in the visible region may be attributed to the Rose Bengal moiety. (The beads are dark red in color.) This conclusion was verified by using a monochromator in several experiments to excite the polymer-sensitizer at 562 nm, the absorption maximum of Rose Bengal.

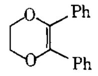
Singlet oxygen undergoes 1,2 cycloaddition with electron-rich alkenes to give 1,2-dioxetanes which cleave thermally to carbonyl-containing products.[3] Photooxidation of



(7)

2,3-diphenyl-*p*-dioxene (**2**)[20] with Ⓟ-Rose Bengal in methylene chloride gave **3** in 95% yield. Absorption spectra of the reaction solution before and after photolysis indicated that no Rose Bengal had leached into the solution during the reaction. The results of several control experiments indicate this to be an authentic singlet oxygen reaction sensitized by the *heterogeneous* sensitizer, Ⓟ-Rose Bengal. The photooxidation of **2** with Ⓟ-Rose Bengal was inhibited by 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher.[21] The reaction was unaffected when conducted in the presence of 2,6-di-*tert*-butylcresol, a free-radical inhibitor. The conversion of **2** to **3** can also be effected by photooxidation with 562-nm radiation using a Bausch and Lomb grating monochromator and SP-200 mercury light source. A suspension of Rose Bengal in CH_2Cl_2 is relatively ineffective in photosensitizing the generation of singlet oxygen. This is probably due to self-quenching in the particles of solid Rose Bengal. The results of these experiments are summarized in Table I.

Table I. Photooxidation of 2,3-Diphenyl-*p*-dioxene (2) with Ⓟ-Rose Bengal in CH_2Cl_2

Expt No.	Reaction conditions[a]	% Reaction After 4 hr
1	 (0.4 mmol) **2** 50 mg of Ⓟ-Rose Bengal	100
2	2 (0.4 mmol) DABCO (0.4 mmol) 50 mg of Ⓟ-Rose Bengal	15
3	2 (0.4 mmol) 2,6-di-*tert*-butyl-*p*-cresol 50 mg of Ⓟ-Rose Bengal	100
4	2 (0.4 mmol) 5 mg of powdered Rose Bengal	4

[a] The reaction mixtures in 10 ml of CH_2Cl_2 were irradiated with a 500-W tungsten–halogen lamp through a uv-cutoff filter.

One criterion for the generation of free singlet oxygen from various sources has been the product distribution obtained from 1,2-dimethylcyclohexene (**4**). Photooxidation of **4** with polymer-based Rose Bengal yields a similar distribution of the two possible ene products **5** and **6** (see Table II).

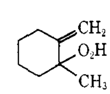
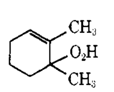
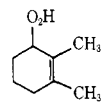
The effect of the amount of Ⓟ-Rose Bengal on the rate of photooxidation of 2,3-diphenyl-*p*-dioxene was investigated (Figure 2). The rate of reaction reached a limiting value which could not be improved upon by introducing additional Ⓟ-Rose Bengal into the reaction. At this point, the intensity of the light source is the limiting factor.

The quantum yield for the production of $^1O_2$ in CH_2Cl_2 with Ⓟ-Rose Bengal has been determined by comparing the rate of photooxidation of **2** in a methanolic solution of Rose Bengal with the rate in CH_2Cl_2 with Ⓟ-Rose Bengal. The steady-state treatment of the kinetic scheme given in eq 1-5 gives the following result:

$$\Phi_{(AO_2)} = \Phi_{(^1O_2)} \frac{k_4[A]}{k_5 + k_4[A]}$$

where $\Phi_{(^1O_2)}$ is the quantum yield for singlet oxygen formation, and $\Phi_{(AO_2)}$ is the quantum yield for product formation.

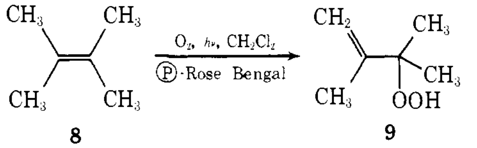
Table II. Oxidation of 1,2-Dimethylcyclohexene (4) Using Various Singlet Oxygen Sources

Sources	 5	 6	 7
Ⓟ-Rose Bengal[a]	87	13	0
Photooxidation (soluble sens)[b]	89	11	0
$OCl^--H_2O_2$ [b]	91	9	0
$(C_6H_5O)_3PO_3$ [c]	96	4	0
K_3CrO_8 [d]	82	18	0
Radical autoxidation[b]	6	39	54

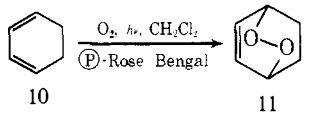
[a] Products from this reaction were analyzed by gas chromatography as the alcohols obtained by triphenylphosphine reduction of 5 and 6. [b] See ref 3a. [c] R. W. Murray, J. W.-P. Lin, and M. L. Kaplan, *Ann. N.Y. Acad. Sci.*, 171, 121 (1970). [d] J. W. Peters, J. N. Pitts, Jr., I. Rosenthal, and H. Fuhr, *Am. Chem. Soc.*, 94, 4348 (1973).

If a relatively reactive acceptor is used in high concentration, $k_4[A] \gg k_5$, the reaction is zero order in [A]; i.e., $\Phi_{(AO_2)} = \Phi_{(^1O_2)}$.[5] Gollnick has reported that $\Phi_{(^1O_2)} = 0.76$ for Rose Bengal in methanol. The quantum yield for the formation of the excited triplet state of Rose Bengal is 0.76.[3c] Therefore, all triplets are quenched to give singlet oxygen. The photooxidation of **2** in methanol with Rose Bengal with 562-nm radiation using a Bausch and Lomb grating monochromator and SP-200 mercury light source followed zero-order kinetics (Figure 3). The conversion of **2** to **3** was monitored by a gas chromatography. Irradiation under identical conditions of a mechanically stirred CH_2Cl_2 solution of **2** with Ⓟ-Rose Bengal gave similar results (Figure 3). In both cases, a second reaction vessel containing **2** in methanol with Rose Bengal was placed behind the vessel being irradiated to establish that all the incident radiation was absorbed by the reaction solution. Least-squares analysis of the data gives zero-order rates for soluble Rose Bengal and Ⓟ-Rose Bengal experiments of 5.08×10^{-8} mol sec^{-1} and 2.88×10^{-8} mol sec^{-1}, respectively. Therefore, $\Phi_{^1O_2}$ (Ⓟ-RB)/$\Phi_{^1O_2}$ (RB in CH_3OH) = 0.57. Using $\Phi_{^1O_2}$ (RB in CH_3OH) = 0.76, $\Phi_{^1O_2}$ (Ⓟ-RB) = 0.43; i.e., the quantum yield for the production of singlet oxygen with the heterogeneous sensitizer, polymer-bound Rose Bengal, is 0.43.

Photooxidation of tetramethylethylene (**8**) in CH_2Cl_2 with Ⓟ-Rose Bengal gave the allylic hydroperoxide **9** in 82% yield. Endoperoxide (**11**) was obtained from 1,3-cyclohexadiene (**10**) in 69% yield under these conditions.



8 **9** (8)



10 11 (9)

Solvents which we have found do not lead to appreciable leaching of the dye from Ⓟ-Rose Bengal include methylene chloride, chloroform, carbon tetrachloride, chlorotrifluoromethane, benzene, toluene, pentane, carbon disulfide, acetone, and methanol.

Other sensitizers that have been attached to the polymer beads include eosin Y (**12**), fluorescein (**13**), chlorophyllin (**14**), and hematoporphyrin (**15**). The results from photooxidation of **2** with these Ⓟ-sens are shown in Table III. While considerably less efficient than the polymer-bound Rose Bengal, the other sensitizers may be of future mechanistic interest. The Ⓟ-chlorophyllin and Ⓟ-hematoporphyrin sensitizers may be particularly valuable in investigations of biological oxidations.

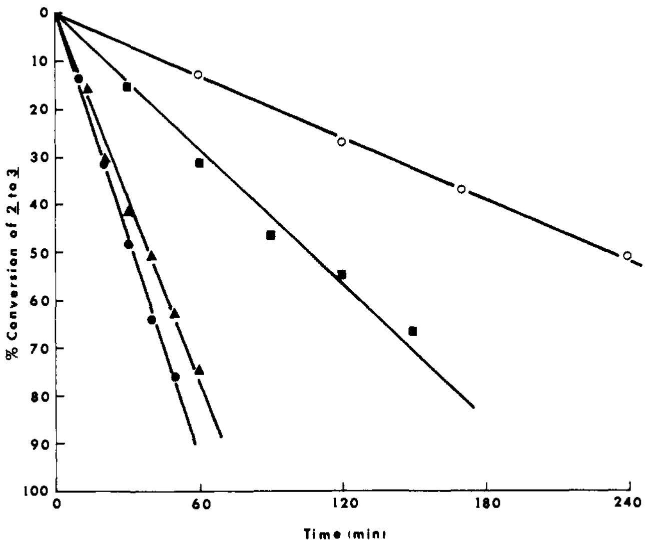
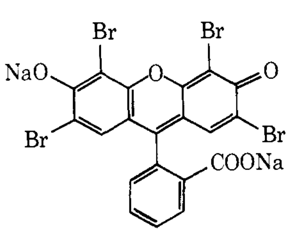


Figure 2. Photooxidation of 2,3-diphenyl-*p*-dioxene (**2**), 3.5×10^{-2} *M*, in 6 ml of CH_2Cl_2, with varying amounts of Ⓟ-Rose Bengal: (●) 75 mg; (▲) 25 mg; (■) 10 mg; (○) 5 mg. Irradiation with a 500-W tungsten-halogen lamp through a uv-cutoff filter.



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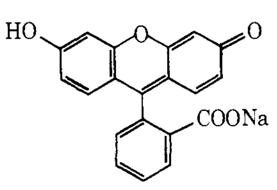

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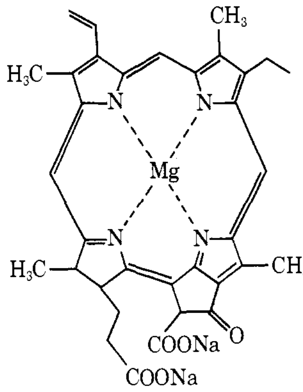

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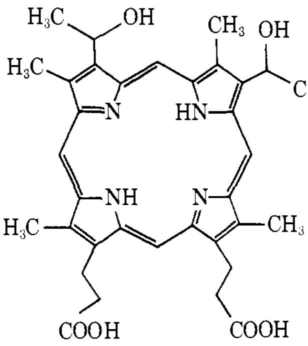

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We have also found that these heterogeneous sensitizers may be used for photooxidations in water. The results of these experiments will be reported separately.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were run on Perkin-Elmer 700 and 337 spectrophotometers. Uv and visible spectra were obtained on a Cary 14 and NMR spectra on Varian T-60 and EM-360 spectrometers. Analytical VPC was performed on a Hewlett-Packard 5750 research gas chromatograph operating in the flame-ionization mode. Analyses were performed by Midwest Micro Labs, Indianapolis, Ind.

Diffuse internal reflectance spectra were measured on a Cary 15 spectrophotometer with an internal reflectance attachment. MgO

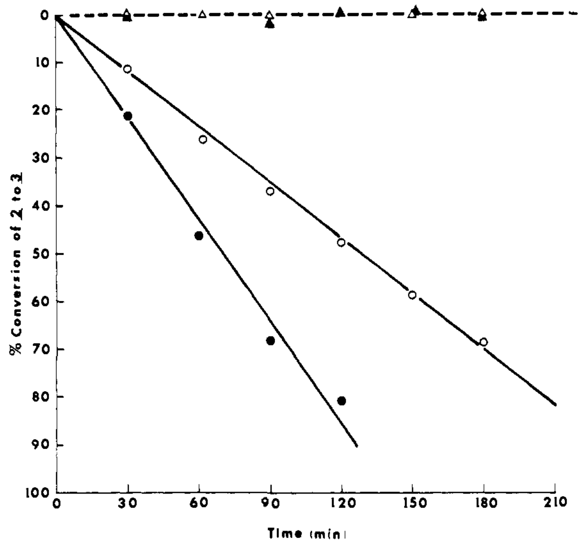

Figure 3. Quantum-yield studies with Ⓟ-Rose Bengal. Photooxidation of 2,3-diphenyl-*p*-dioxene (**2**) with 562-nm radiation: (●) reaction solution with 2.93×10^{-2} *M* **2** and 2.73×10^{-4} *M* Rose Bengal in methanol; (▲) rear control solution with 2.93×10^{-2} *M* **2** and 2.73×10^{-4} *M* Rose Bengal in methanol; (○) reaction solution with 2.99×10^{-2} *M* **2** and 200 mg Ⓟ-Rose Bengal in 15 ml of CH_2Cl_2; (△) rear control solution with 3.06×10^{-2} *M* **2** and 2.73×10^{-4} *M* Rose Bengal in methanol.

was used as the suspending agent, and concentrations were approximately 0.002 mol of reflecting entity per mole of MgO. The data in Figure 1 are the reflectance spectra of solid Rose Bengal and of polymer-based Rose Bengal under identical conditions.

Chloromethylated styrene-divinylbenzene copolymer beads were obtained from Bio-Rad Laboratories (SX-1). The following alkenes were obtained for use as substrates: 2,3-diphenyl-*p*-dioxene (mp 94.5-95°),[22] 1,3-cyclohexadiene (Aldrich), tetramethylethylene (Aldrich), and 1,2-dimethylcyclohexene (Chemical Samples Co.).

General Procedure for Preparation of Polymer-Bound Sensitizers. To 2.0 g of chloromethylated styrene-divinylbenzene copolymer beads (Bio-Rad SX-1, 1.11 mequiv of Cl/g of polymer) in 60 ml of dimethylformamide[23] was added 1.55 mmol of sensitizer. The mixture was stirred magnetically and heated (60°)[24] for 20 hr. The reaction mixture was then cooled to ambient temperature and filtered through a sintered-glass funnel. The residue was washed thoroughly with 200-ml portions of solvent in the following order: ethyl acetate, ethanol, ethanol-water (1:1), water, methanol-water (1:1), and methanol. The polymer beads were then extracted with methylene chloride and methanol in a Soxhlet extractor for at least 20 hr until no visible color appeared in the solvent. The polymer-sensitizer was then dried in a vacuum oven at 60° for 12 hr.

Characterization of Ⓟ-Rose Bengal. The polymer-bound Rose Bengal, prepared as described above, was analyzed by combustion for iodine content in order to determine the percent reaction of the chloromethyl groups with Rose Bengal. The data given in Table IV indicate that 16.5% of the chloromethyl groups had been converted to the Rose Bengal derivative. This Ⓟ-Rose Bengal was used in the photooxidations.

Cleavage of Ⓟ-Rose Bengal. To 10 ml of trifluoroacetic acid (TFA) was added 200 mg of Ⓟ-Rose Bengal (from Ⓟ-CH_2Cl containing 0.69 mequiv of Cl/g of polymer). Anhydrous hydrogen bromide gas was bubbled into the reaction vessel for 45 min at room temperature. The flask was stoppered and allowed to stand for 16 hr at room temperature. The polymer beads were then removed by filtration followed by washing three times with TFA. The filtrate was evaporated under reduced pressure at 50°. The residue, a slightly yellow semisolid, weighed 6.8 mg. Addition of a few drops of 5% sodium hydroxide solution gave a rose colored solution with a λ_{max} 555 nm.[25] The weight of recovered Rose Bengal indicated incomplete cleavage from the polymer. The recovered polymer was then treated further with 250 mg of potassium hydroxide in 10 ml of methanol with stirring at room temperature for 24 hr. The mixture was filtered and washed with methanol. The total filtrate was transferred into a volumetric flask and diluted to 100 ml with methanol. The visible spectrum of the solution showed a maximum absorption at 555 nm (A = 1.62 corresponding to 3.8 mg of free Rose Bengal). The total recovered Rose Bengal from the acidic and basic hydrolysis was 10.6 mg (0.0534 mmol/g of Ⓟ-Rose Bengal).

Table III. Photooxidation of 2,3-Diphenyl-*p*-dioxene (**2**) with Various Ⓟ-sens[a]

Ⓟ-sens	λ_{max} of soluble sens (solvent)	Time required for 50% conversion of 2 to 3 (min)
Rose Bengal	562 (acetone)	39
Eosin Y	520 (water)	87
Fluorescein	493 (water)	350
Chlorophyllin	440 (hexane)	285
Hematoporphyrin	494 (ethanol)	590

[a] All experiments were conducted with 25 mg of Ⓟ-sens and 50 mg of **2** in 6 ml of CH_2Cl_2 with irradiation from a 500-W tungsten-halogen lamp through a uv-cutoff filter.

Table IV. Analysis of Ⓟ-Rose Bengal

Ⓟ-CH_2Cl (mequiv of Cl/ g of polymer)	Combustion analysis,[a] % I	Attached Rose Bengal (mmol of Rose Bengal/ g of polymer)
1.11	9.36	0.183

[a] Average of duplicate analyses.

Photooxidation Procedure. The photooxidations were carried out in a 2-cm square Pyrex tube equipped with a glass paddle which was driven from above by an attached, glass-enclosed, bar magnet. Oxygen was passed over the surface of the agitated solution during the irradiations. The light source for the preparative experiments consisted of a 500-W tungsten-halogen lamp (GE Q500Cl) with a uv-cutoff filter (Corning 3060: transmission 365 nm = 0.5%).

Photooxidation of 2,3-Diphenyl-*p*-dioxene (2) with Ⓟ-Rose Bengal. 2,3-Diphenyl-*p*-dioxene (**2**) (97.5 mg, 0.4 mmol) was dissolved in 10 ml of dry CH_2Cl_2 and added with 50 mg of Ⓟ-Rose Bengal to the irradiation vessel. The conversion of **2** to ethylene glycol dibenzoate (**3**) was followed by VPC (10-ft 20% Apiezon L at 250°). After 4 hr, the Ⓟ-Rose Bengal was filtered from the solution, and a uv-visible spectrum was recorded. The filtrate showed no absorption between 450 and 800 nm. The filtered CH_2Cl_2 solution (slightly yellow) was stripped of solvent, and the oxidation product **3** [mp 70-71° (lit.[26] 73°)] was isolated in 95% yield.

Photooxidation of 2,3-Diphenyl-*p*-dioxene (2) in the Presence of 2,6-Di-*tert*-butyl-*p*-cresol. 2,3-Diphenyl-*p*-dioxene (**2**) (96.3 mg, 0.4 mmol) was dissolved in 10 ml of dry CH_2Cl_2. 2,6-Di-*tert*-butyl-*p*-cresol (0.04 mmol) and Ⓟ-Rose Bengal (50 mg) were added, and the sample was irradiated for 4 hr. VPC analysis of the reaction mixture indicated complete conversion to ethylene glycol dibenzoate (**3**) in this time period.

Photooxidation of 2,3-Diphenyl-*p*-dioxene (2) in the Presence of 1,4-Diazabicyclo[2.2.2]octane (Dabco). 2,3-Diphenyl-*p*-dioxene (**2**) (97.3 mg, 0.4 mmol) was dissolved in 10 ml of dry CH_2Cl_2. DABCO (0.4 mmol) and 50 mg of Ⓟ-Rose Bengal were added, and the sample was irradiated for 4 hr. VPC analysis of the reaction mixture indicated only 15% conversion to **3**.

Photooxidation of 2,3-Diphenyl-*p*-dioxene (2) with Rose Bengal in Suspension. 2,3-Diphenyl-*p*-dioxene (**2**) (95.81 mg, 0.4 mmol) was dissolved in 10 ml of dry CH_2Cl_2, and 5 mg of Rose Bengal was added. The *suspension* obtained was intensely red. Irradiation of the suspension for 4 hr followed by filtration through a sintered-glass filter afforded a colorless solution. VPC analysis of the filtrate indicated only 4% conversion to **3**.

Photooxidation of 2,3-Diphenyl-*p*-dioxene (2) with Ⓟ-Rose Bengal Using Monochromatic Light. 2,3-Diphenyl-*p*-dioxene (**2**) (51 mg, 0.21 mmol) was dissolved in 6 ml of dry CH_2Cl_2, and 50 mg of Ⓟ-Rose Bengal was added. The solution was irradiated at 565 nm with a Bausch and Lomb grating monochromator with an SP-200 mercury light source. VPC analysis of the reaction mixture showed that the starting material was completely consumed in 2 hr. Examination of the uv-visible spectrum of the filtered reaction solution showed no absorptions in the 450–800 nm region.

Photooxidation of 1,2-Dimethylcyclohexene with Ⓟ-Rose Bengal. 1,2-Dimethylcyclohexene (**4**) (0.1191 g, 1.08 mmol) in 10 ml of CH_2Cl_2 and Ⓟ-Rose Bengal (200 mg) was irradiated with the tungsten-halogen lamp for 4.5 hr. The resulting hydroperoxides were reduced with an excess of triphenylphosphine to the corresponding alcohols. VPC analysis of the allylic alcohols was effected using a 10 ft 20% Carbowax 20M column at 130°. The yields of cyclohexenol products are reported in Table II. Authentic samples of the alcohols **5** and **6** were obtained by photooxidation of **4** with soluble sensitizer.[3a]

Photooxidation of Tetramethylethylene (8) with Ⓟ-Rose Bengal. Tetramethylethylene (**8**) (0.50 g, 6.0 mmol) in 10 ml of CH_2Cl_2 and Ⓟ-Rose Bengal (100 mg) was irradiated under O_2 with the tungsten-halogen lamp. VPC analysis showed the reaction to be complete after 10 hr. The Ⓟ-Rose Bengal was filtered from the reaction solution, and the CH_2Cl_2 was stripped off. Distillation of the residue under vacuum through a short-path column {bp 58° (12 mm) [lit.[27] bp 55° (12 mm)]} gave 82% of the allylic hydroperoxide **9**.

Photooxidation of 1,3-Cyclohexadiene (10) with Ⓟ-Rose Bengal. 1,3-Cyclohexadiene (**10**) (0.50 g, 6.3 mmol) in 10 ml of CH_2Cl_2 and 200 mg of Ⓟ-Rose Bengal was irradiated for 9.5 hr with the tungsten-halogen lamp. The Ⓟ-Rose Bengal was filtered off and the CH_2Cl_2 stripped from the crude product. The crude endoperoxide **11** was distilled under vacuum [bp 84° (2 mm)], and the resulting pale-yellow oil was recrystallized from pentane to yield white crystals in 69% yield: mp 90–91° (lit.[28] 88.5°); ^1H NMR (CCl_4-Me_4Si) δ 1.70 (m, 4 H), 4.45 (broad s, 2 H), and 6.55 (m, 2 H). The ^1H NMR data are in agreement with the values reported by Foote and Wexler.[5]

Quantum Yield for Singlet Oxygen Formation with Ⓟ-Rose Bengal in CH_2Cl_2. The quantum yield for $^1O_2$ formation with Ⓟ-Rose Bengal in CH_2Cl_2 was determined by comparing the rate of photooxidation of 2,3-diphenyl-*p*-dioxene (**2**) with Ⓟ-Rose Bengal in CH_2Cl_2 with the rate obtained with Rose Bengal dissolved in methanol. The quantum yield for $^1O_2$ formation with Rose Bengal in methanol is 0.76.[3c]

A solution of **2** (0.029 *M*) and Rose Bengal (2.7×10^{-4} *M*) in CH_3OH was prepared. Irradiation of 6 ml of this solution in the square Pyrex cell under O_2 with 562-nm light led to the formation of ethylene glycol dibenzoate (**3**). VPC analysis of the photooxidation gave the results shown in Figure 3. Under these conditions, the rate of photooxidation of **2** was 5.08×10^{-8} *M* sec^{-1}. In order to ensure that all the incident radiation had been absorbed by the reaction solution, a second square Pyrex cell containing 4 ml of the above solution of **2** and Rose Bengal was placed behind the reaction vessel. VPC analysis indicated that no photooxidation occurred in the second cell.

The rate of photooxidation of **2** with Ⓟ-Rose Bengal in CH_2Cl_2 was determined as above. A 6-ml solution of **2** (0.029 *M*) in CH_2Cl_2 with 200 mg of Ⓟ-Rose Bengal was irradiated under O_2 with 562-nm light. Stirring was continued throughout the photooxidation. The progress of the reaction was monitored by VPC. The rate of photooxidation of **2** with Ⓟ-Rose Bengal in CH_2Cl_2 under these conditions was 2.88×10^{-8} *M* sec^{-1} (Figure 3). Again to ensure that all the incident radiation had been absorbed by the reaction solution containing the heterogeneous sensitizer, a second cell with 4 ml of the methanolic solution of **2** and Rose Bengal was placed behind the reaction vessel. VPC analysis showed no photooxidation in the second cell. Comparison of these zero-order rates of photooxidation gave a quantum yield for $^1O_2$ formation with Ⓟ-Rose Bengal in CH_2Cl_2 of 0.43.

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References and Notes

(1) Preliminary results were reported in communication form: E. C. Blossey, D. C. Neckers, A. L. Thayer, and A. P. Schaap, *J. Am. Chem. Soc.*, **95**, 5820 (1973).

(2) (a) Alfred P. Sloan Research Fellow, 1974–1976, Wayne State University; (b) Wayne State University; (c) Rollins College, Winter Park, Fla.; (d) Alfred P. Sloan Research Fellow, 1971–1973, Bowling Green State University, Bowling Green, Ohio.

(3) (a) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968); (b) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (c) K. Gollnick and G. O. Schenck in "1,4-Cycloaddition Reactions", J. Hammer, Ed., Academic Press, New York, N.Y., 1967, p 255; (d) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968); (e) W. R. Adam in "Oxidation", Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N.Y., 1971, p 65; (f) T. Wilson and J. T. Hastings, *Photophysiology*, **5**, 49 (1970); (g) R. W. Denny and A. Nickon in "Organic Reactions", Vol. 20, W. G. Dauben, Ed., Wiley, New York, N.Y., 1973, p 133.

(4) (a) H. Kautsky and H. deBruijn, *Naturwissenschaften*, **19**, 1043 (1931); (b) H. Kautsky, *Biochem. Z.*, **291**, 271 (1937).

(5) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968).

(6) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **90**, 4161 (1968).

(7) M. E. Brennan, *Chem. Commun.*, 956 (1970).

(8) A. P. Schaap, K. Kees, and A. L. Thayer, Abstracts, 6th Central Regional Meeting of the American Chemical Society, Detroit, Mich., April 1974; A. P. Schaap, K. Kees, and A. L. Thayer, *J. Org. Chem.*, **40**, 1185 (1975).

(9) H. H. Wasserman and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 3073 (1967).

(10) M. Kasha and A. U. Khan, *Ann. N.Y. Acad. Sci.*, **171**, 5 (1970).

(11) J. W. Peters, J. N. Pitts, Jr., I. Rosenthal, and H. Fuhr, *J. Am. Chem. Soc.*, **94**, 4348 (1972).

(12) E. J. Corey and W. C. Taylor, *J. Am. Chem. Soc.*, **86**, 3881 (1964).

(13) K. Goda, J. Chu, T. Kimura, and A. P. Schaap, *Biochem. Biophys. Res. Commun.*, **52**, 1300 (1973).

(14) (a) J. Stauff, *Photochem. Photobiol.*, **4**, 1199 (1965); (b) R. M. Arneson, *Arch. Biochem. Biophys.*, **136**, 352 (1970).

(15) R. M. Howes and R. H. Steele, *Res. Commun. Chem. Pathol. Pharmacol.*, **3**, 349 (1972).

(16) R. C. Allen, R. L. Stjernholm, and R. H. Steele, *Biochem. Biophys. Res. Commun.*, **47**, 679 (1972).

(17) Williams and coworkers have reported the use of several complexes of dyes with ion-exchange resins for the photochemical generation of $^1O_2$: J. R. Williams, G. Orton, and L. R. Unger, *Tetrahedron Lett.*, 4603, (1973).

(18) Nilsson and Kearns have recently described experiments with sensitizers adsorbed on silica gel particles: R. Nilsson and D. R. Kearns, *Photochem. Photobiol.*, **19**, 181 (1974).

(19) R. B. Merrifield, *Science*, **150**, 178 (1965).

(20) (a) A. P. Schaap, *Tetrahedron Lett.*, 1757 (1970); (b) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N.Y. Acad. Sci.*, **171**, 79 (1970).

(21) C. Ouannès and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6527 (1968).

(22) R. K. Summerbell and D. R. Berger, *J. Am. Chem. Soc.*, **81**, 633 (1959).

(23) Purified according to J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis", W. F. Freeman, San Francisco, Calif., 1969, p 31.

(24) Except for chlorophyllin and hematoporphyrin which were reacted at room temperature.

(25) Rose Bengal under these conditions gave the same absorption maximum.

(26) E. J. Bourne, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

(27) G. O. Schenck and K. H. Schulte-Elte, *Justus Liebigs Ann. Chem.*, **618**, 185 (1958).

(28) G. O. Schenck and W. Willmund, reported by R. Criegee in Houben-Weyl, "Methoden der Organischen Chemie", Vol. VIII, 4th ed, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1952, p 16.