62415-98-9; 4,4′-DPyE *r-tct* dimer, 73078-76-9; *trans*-3,2′-PyPaE, 73048-52-9; *cis*-3,2′-PyPaE, 73048-62-1; *r*-1,*c*-2,*t*-3,*t*-4-tetra(2-pyrazinyl)cyclobutane, 73069-94-0; *r*-1,*t*-3-di(3-pyridyl)-*c*-2,*t*-4-di(2-pyrazinyl)cyclobutane, 73078-81-6; *r*-1,*c*-2-di(3-pyridyl)-*t*-3,*t*-4-di(2-pyrazinyl)cyclobutane, 73069-95-1; *trans*-2,2′-DPaE, 62141-47-3; *trans*-4,4′-DiQE, 73048-54-1; *trans*-2,4′-PaiQE, 73048-58-5; *trans*-3,4′-PyiQE, 73048-57-4; *trans*-4,4′-DPyE 2CH$_3$I, 24274-78-0; *trans*-2,2′-DPyE 2CH$_3$I, 73048-55-2; *trans*-2,2′-DPyE (CH$_3$)$_2$SO$_4$, 73048-66-5; *trans*-2,2′-DPyE CH$_3$I, 73048-56-3; *trans*-4,4′-DPyE (CH$_3$)$_2$SO$_4$, 73048-65-4; *trans*-4,4′-DPyE CH$_3$BF$_4$, 73069-97-3; *trans*-4,4′-DPyE CH$_3$I, 73048-64-3; 3,4′-PyiQE *r-ctt hth* dimer, 73069-98-4; 3,4′-PyiQE *r-tct hth* dimer, 73089-62-0; 3,4′-PyiQE *r-ctt htt* dimer, 73069-99-5; 2,4′-PaiQE *r-ctt hth* dimer, 73070-00-5; 2,3-di(2-pyridyl)propanol, 73070-01-6; 1,2-di(4-pyridyl)ethane, 4916-57-8; 2,3-di(4-pyridyl)propanol, 73070-02-7; 4,4′-DPyE·(MeO)$_2$SO$_2$ *r-ctt* dimer, 73070-04-9; 1,2-di(2-pyridyl)ethane, 4916-40-9.

Supplementary Material Available: Results and discussion of the X-ray structure determination of five azastilbene dimers plus full X-ray data for these compounds. (17 pages). Ordering information is given on any current masthead page.

Polymer-Based Sensitizers for Photochemical Reactions. Silica Gel as a Support

Seizo Tamagaki, Cathy E. Liesner, and Douglas C. Neckers*

Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403

Received October 2, 1979

Silica gel has been converted to silylated derivatives which can be converted to sensitizers for singlet oxygen formation. The silica gel sensitizers, [P$_{\mathrm{Si}}$]-rose bengals,[1] are versatile and useful in both polar and nonpolar media. [P$_{\mathrm{Si}}$]-Rose bengal has been studied as a source of singlet oxygen and its uses in reactions of sulfite ion, tryptophan, and 2,3-diphenyldioxene are reported. Results are compared with unbound and polystyrene-based rose bengal ([P]-rose bengal).

Silica gel has attracted considerable attention in the petroleum industry as a low cost support for the anchoring of heavy metal catalysts. In view of our continuing interest in the use of polymers in organic photochemical synthesis[2] and in view of our already described supported reagent for singlet oxygen genesis based on styrene–divinylbenzene copolymer beads,[3a] the development of a polymer-supported sensitizer for singlet oxygen genesis in which the polymer support was solvent versatile, rather than solvent limited, seemed obvious.

Accordingly, we have developed a pair of sensitizers for singlet oxygen formation: [P$_{\mathrm{Si}}$]-rose bengal and [P$_{\mathrm{Cl}}$]-rose bengal, the former supported on silica gel, the latter supported on cellulose. Silica gel adsorbed (in contrast to covalently attached) sensitizers have been studied before[3b] and have been acknowledged to have numerous disadvantages;[4] therefore the silica gel bound materials were designed to add the versatility of the support to the stability of the bound reagent.

Silica gel rose bengal, [P$_{\mathrm{Si}}$]-rose bengal, was prepared by the following reactions:

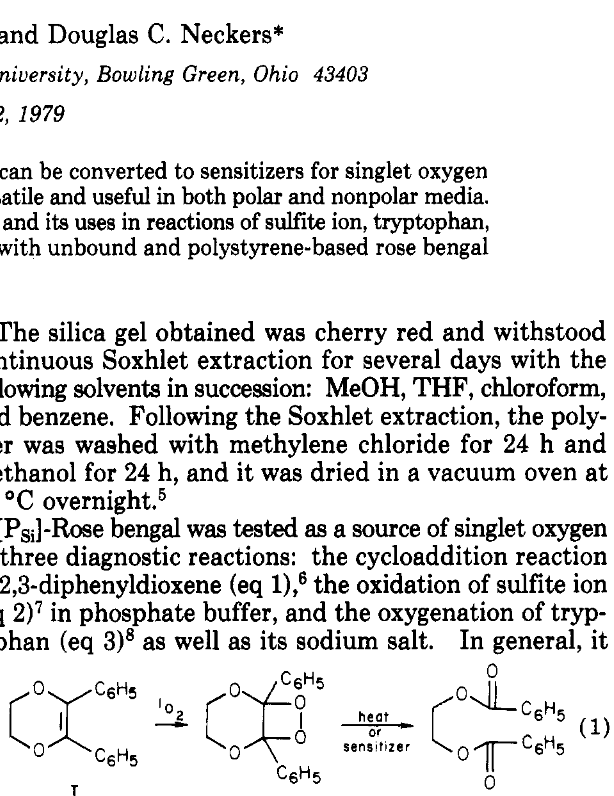
$$\mathrm{Cl_3Si(CH_2)_3Cl + EtOH \xrightarrow[C_6H_6]{Et_3N} (EtO)_3Si(CH_2)_3Cl}$$

$$\mathrm{[P_{Si}]\text{-}OH + (EtO)_3Si(CH_2)_3Cl \xrightarrow[150\ ^\circ C]{xylene} [[P_{Si}]\text{-}O]_3Si(CH_2)_3Cl}$$

$$\mathrm{[[P_{Si}]\text{-}O]_3Si(CH_2)_3Cl + rose\ bengal \xrightarrow[135\ ^\circ C]{DMF} [[P_{Si}]\text{-}O]_3Si(CH_2)_3\text{-}rose\ bengal}$$

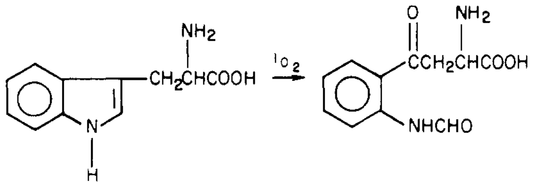
The silica gel obtained was cherry red and withstood continuous Soxhlet extraction for several days with the following solvents in succession: MeOH, THF, chloroform, and benzene. Following the Soxhlet extraction, the polymer was washed with methylene chloride for 24 h and methanol for 24 h, and it was dried in a vacuum oven at 50 °C overnight.[5]

[P$_{\mathrm{Si}}$]-Rose bengal was tested as a source of singlet oxygen in three diagnostic reactions: the cycloaddition reaction of 2,3-diphenyldioxene (eq 1),[6] the oxidation of sulfite ion (eq 2)[7] in phosphate buffer, and the oxygenation of tryptophan (eq 3)[8] as well as its sodium salt. In general, it is observed that [P$_{\mathrm{Si}}$]-rose bengal is as effective as is [P]-rose bengal in forming singlet oxygen in nonpolar solvents, but unlike [P]-rose bengal, which one would expect to agglomerate in water because of the hydrophobicity



I II III (1)

$$\mathrm{SO_3{}^{2-} \xrightarrow[{}^1O_2]{} SO_4{}^{2-}} \tag{2}$$



(3)

---

(1) The common symbol for polymer support systems, circled characters, has been replaced by brackets because of composition difficulties.

(2) For leading references to our work see (a) Blossey, E. C.; Neckers, D. C. "Benchmarks in Photochemistry"; Dowden, Hutchinson, and Ross: Stroudsburg, PA; (b) Neckers, D. C. *CHEMTECH* **1978**, *8*, 108; (c) Card, R. J.; Neckers, D. C. *Isr. J. Chem.* **1979**, *17*, 269.

(3) (a) Marketed under the trade name "Sensitox", Hydron Laboratories, New Brunswick, NJ. (b) Williams, J. R.; Orton, G.; Unger, L. R. *Tetrahedron Lett.* **1973**, 4303. Takeshita, H.; Hatsui, T. *J. Org. Chem.* **1978**, *43*, 3081.

(4) Srinivasan, V. S.; Neckers, D. C. unpublished results. Blossey, E. C.; Neckers, D. C., unpublished results.

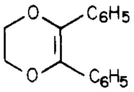
(5) It was also possible to prepare a silica gel rose bengal by the reaction of silica gel first with thionyl chloride, and then with rose bengal. This silica gel rose bengal was not as stable to hydrolysis as that described above, so it was tested as a source of singlet oxygen (which it is) and then not further utilized.

(6) Bartlett, P. D.; Mendenhall, G. D.; Schaap, A. P. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 79.

(7) (a) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1969**, *244*, 6056. (b) Misra, H. P.; Fridovich, I. *Ibid.* **1972**, *247*, 3170.

(8) (a) Fontana, A.; Toniolo, C. *Proc. Chem. Org. Nat. Prod.* **1974**, *33*, 309. (b) Sakiyama, F.; Masuda, N. *Photochem. Photobiol.* **1974**, *19*, 115.

0022-3263/80/1945-1573$01.00/0 © 1980 American Chemical Society

Table I. Photooxidation of  **(200 mg) in 40 mL of CH_2Cl_2**

			products, %[a]		
			I	II	III
(1)	$[P_{Si}]$-RB 200 mg (1.3 RB mg/g)	$\xrightarrow{6\ h,\ h\nu}$	0	0	100
(2)	[Cl]-RB[c] 100 mg (0.7 mg/g)	$\xrightarrow{5\ h,\ h\nu}$	64	0	30
(3)	[P]-CH_2RB 50 mg (0.76 mg of RB/g)	$\xrightarrow[h\nu]{20\ min}$	53	42	5
(4)	[P]-CH_2RB 50 mg	$\xrightarrow[h\nu]{5\ h}$	0	8	92
(5)	[P]-CH_2RB 50 mg	$\xrightarrow[\text{in the presence of silica gel (500 mg)}]{2\ h,\ h\nu}$	0	87	13

[a] I = recovered 2,3-diphenyldioxene, II = 2,3-diphenyldioxene dioxetane, III = ethylene glycol dibenzoate. [b] Prepared by method II. [c] [Cl]-RB is cellulose rose bengal prepared by chlorination and the reaction with rose bengal according to procedure II.

Table II. $[P_{Si}]$-Rose Bengal as a Source of Singlet Oxygen in Various Solvents: Oxidation of 2,3-Diphenyldioxene[a,b]

solvent	I, %	II, %	III, %
MeOH-CH_2Cl_2 (3:1)	51	15	34
MeOH-THF	55	27	18
H_2O-THF	49	11	40
acetone	26	27	7
benzene	24	65	11
pentene	23	42	35
CH_3CN	22	74	4
CH_2Cl_2	17	74	7
CCl_4	10	77	13
CS_2	6	66	28

[a] I, II, and III are the same as in Table I. [b] 200 mg of $[P_{Si}]$-rose bengal (6.6 mg/g silica gel), time = 2 h, 200 mg of 2,3-diphenyl-*p*-dioxene, 50 mL of solvent, temperature = 10 ± 1 °C.

of the styrene–divinylbenzene polymer on which it is based, $[P_{Si}]$-rose bengal functions in aqueous solution as effectively as does rose bengal itself.

The photooxidation of 2,3-diphenyldioxene was carried out with $[P_{Si}]$-rose bengal in CH_2Cl_2 at room temperature under conditions of oxygen saturation. The results are shown in Table I where they are also compared with [P]-rose bengal. The reaction was solvent dependent (see Table II) and that solvent dependency paralleled the lifetime of singlet oxygen[9] in the solvents in question. In hydroxylic solvents where the lifetime of $^1O_2$ is short, conversion to the dioxetane (II) and dibenzoate (III) is lower than in nonpolar solvents. The reaction of 2,3-diphenyldioxene with singlet oxygen from $[P_{Si}]$-rose bengal was completely quenched with 1,4-diazabicyclo[2.2.2]octane (Dabco) (Table III) but was unaffected by 2,6-di-*tert*-butylcresol, a known free-radical inhibitor.

Two products were readily observed from the reaction of 2,3-diphenyldioxene with $[P_{Si}]$-rose bengal, the dioxetane and the ring-opened dibenzoate ester (eq 1). As is readily apparent from Tables I–III, the ratio of the two products was also solvent dependent, though the dibenzoate was present in greater quantities in the absence of the radical inhibitor (Table III).

$[P_{Si}]$-Rose bengal could be recycled and reused for several successive oxidations both in methylene chloride (Table IV) and in the more polar MeOH–methylene chloride mixture (Table V). Under the latter conditions, [P]-rose bengal is not useful because as a hydrophobic polymer, it agglomerates. Its rate of bleaching is also enhanced in polar solvents.

Table III. $[P_{Si}]$-Rose Bengal as a Source of Singlet Oxygen: Inhibition by 2,6-Di-*tert*-butylcresol and Dabco[a]

solvent	I	II	III	conditions
MeOH-CH_2Cl_2 (3:1)	59	23	18	inhibited by 2,6-di-*tert*-butylcresol
	(51)	(15)	(34)	uninhibited
CH_2Cl_2	25	62	13	inhibited by 2,6-di-*tert*-butylcresol
CH_2Cl_2	99		1	0.1 mol of Dabco
CH_2Cl_2	(17)	(74)	(9)	uninhibited

[a] 200 mg of $[P_{Si}]$-rose bengal (6.6 mg/g silica gel), time = 2 h, 200 mg of 2,3-diphenyl-*p*-dioxene, 50 mL of solvent, temperature = 10 ± 1 °C.

Table IV. Recycling $[P_{Si}]$-Rose Bengal:[a] Oxidation of 2,3-Diphenyldioxene

		products, % yield		
run	wt,[b] mg	I	II	III
1	200	17	74	1
2	185	7	82	11
3	170	4	83	13
4	168	10	70	20
5	145	10	72	18

[a] Prepared by general procedure I; solvent CH_2Cl_2. [b] Sensitizer was recovered and used again in the same system; temperature = 10 ± 1 °C, 200 mg of 2,3-diphenyldioxene, 2-h irradiation, 50 mL of CH_2Cl_2.

The photooxidation of 2,3-diphenyldioxene with [P]-rose bengal is compared in Table VI under identical conditions of irradiation with that with $[P_{Si}]$-rose bengal, and similar results for unbound rose bengal are also included for comparison (Table VII). In polar solvents, such as MeOH–THF, or in THF the reaction is faster with $[P_{Si}]$-rose bengal.

The photooxidation of sulfite has been shown to be a diagnostic test of extraordinary sensitivity for the presence of superoxide ion.[10] There is a ground-state autoxidation

---

(9) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 1029.

(10) Fridovich, I. *Acc. Chem. Res.* **1977**, *10*, 346.

Table V. Recycling [P_{Si}]-Rose Bengal: Oxidation of 2,3-Diphenyldioxene[a]

		products, % yield		
run	wt, mg	I	II	III
1	200	51	11	34
2	195	35	25	40

[a] Solvent CH_2Cl_2-MeOH (1:1). Sensitizer was recovered and used again in the same system. Products I, II, and III are the same as in Table I; temperature = 10 ± 1 °C, 200 mg of 2,3-diphenyldioxene, 2-h irradiation, 50 mL of solvent.

Table VI. Photooxidation of 2,3-Diphenyldioxene Using [P]-Rose Bengal[a] in Several Solvents[c]

	% yield of product		
solvent	I	II	III
CS_2 (bleached)	99	1^b	1^b
pentane	98	0	2
CH_3CN	98	2^b	2^b
	97	3^b	3^b
MeOH-THF	93	5	2
THF	85	12	3
benzene	80	17	3
H_2O-THF	72	22	6
acetone	66	28	6
CH_2Cl_2	52	38	10
CH_2Cl_2	44	44	12

[a] Styrene-2% divinylbenzene, 50 mg of [P]-rose bengal (6.5 mg/g), 50 mL of solvent, 200 mg of 2,3-diphenyl-*p*-dioxene, 10 ± 1 °C, 2 h. I = 2,3-diphenyldioxene recovered; II = 2,3-diphenyldioxene dioxetane; III = ethylene glycol dibenzoate. [b] Combined yield for both products II and III. [c] See also Figure 2.

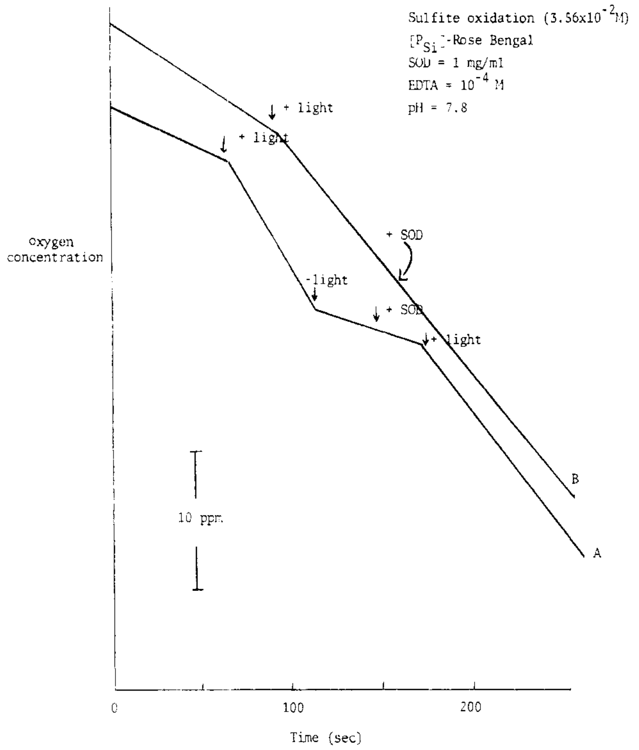


Figure 1. Photooxidation of sulfite with [P_{Si}]-rose bengal. Broad spectrum visible light source, UV cutoff filter. (Curve A) At the first arrow the light source was turned on; at the second arrow the light source was turned off; at the third arrow superoxide dismutase was injected; at the fourth arrow the light was turned back on. (Curve B) At the first arrow the light was turned on; at the second arrow superoxide dismutase was injected.

Table VII. Photooxidation of 2,3-Diphenyldioxene Using Unbound Rose Bengal[a]

	I	II	III
CS_2[b,c]	99		
pentane[c]	99		
CH_2Cl_2[c]	98		
CH_3CN	31	54	15
acetone	31	63	6
MeOH-CH_2Cl_2	24	42	34

[a] 0.28 mg in 40 mL of solvent. [b] Note: rose bengal is not soluble in CS_2, pentane, or CH_2Cl_2. [c] In this solvent the rose bengal bleached colorless; I, II, III same as in Table VI; 200 mg of 2,3-diphenyldioxene, 10 ± 1 °C, 2 h.

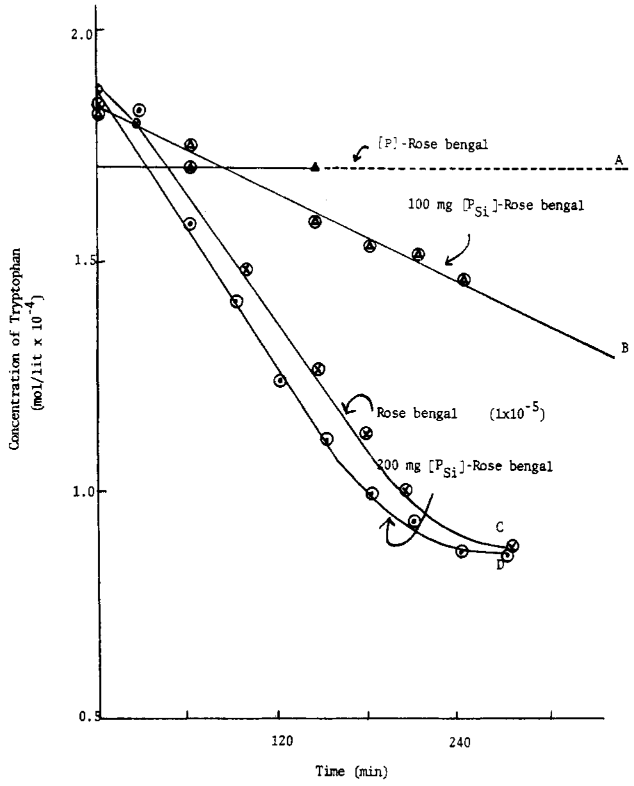


Figure 2. Photooxidation of tryptophan in water using [P_{Si}]-rose bengal. Photooxidation of tryptophan in water: (curve A) 200 mg of [P]-rose bengal; (curve B) 100 mg of [P_{Si}]-rose bengal added; (curve c) 1×10^{-5} M rose bengal added; (curve d) 200 mg of [P_{Si}]-rose bengal added.

reaction which is a chain process that can be prevented with suitable free-radical inhibitors. The photooxidation is also inhibited by singlet oxygen quenchers and by superoxide dismutase, a known quencher of superoxide. Thus rose bengal in aqueous solution has been shown to be not only a source of singlet oxygen but also a source of superoxide ion in the presence of sulfite ion.[11]

The photooxygenation of sulfite with [P_{Si}]-rose bengal is shown in Figure 1 in the presence of quantities of superoxide dismutase. Superoxide dismutase has no effect on the rate of oxidation. The implication is that [P_{Si}]-rose bengal produces much less (if any within experimental detection limits) superoxide ion photochemically than does rose bengal alone, under these conditions, i.e., in aqueous solution with sulfite as the accepting substrate.

The results of oxygenation of tryptophan in water using [P_{Si}]-rose bengal are shown in Figure 2. Tryptophan photooxidizes[12] to give *N*-formylkynurenine (eq 3), a

---

(11) Srinivasan, V. S.; Podolsky, D.; Westrick, N.; Neckers, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 6513.

(12) Saito, I.; Matsuura, T.; Nakagawa, M.; Hino, T. *Acc. Chem. Res.* **1977**, *10*, 346.

known metabolite of the amino acid.[12] Under the conditions of this oxygenation, [P]-rose bengal gave no detectable photooxidation, though rose bengal itself is an efficient sensitizer. The reaction rate with $[P_{Si}]$-rose bengal (200 mg; 6.6 mg/g) is quite comparable to that with the sensitizer alone.

Heterogeneous sensitization is obviously the easiest way to carry out a synthetic photooxidation. The heterogeneous sensitizer facilitates the separation of sensitizer from product, thus reducing the number of separation steps necessary in the overall synthetic process.

In our most recent experience, however, $[P_{Si}]$-rose bengal has advantages over either rose bengal or [P]-rose bengal in singlet oxygenation in polar solvents. One advantage has to do with its inability to form superoxide ion, something which is not the case when rose bengal is used by itself in aqueous solution—at least with SO_3^{2-} as the substrate. Another advantage is its versatility—it can be used in both nonpolar and polar solvents. Perhaps the most obvious reason to use $[P_{Si}]$-rose bengal is the simplicity of its synthesis and use. As such it offers an alternative to the recently reported commercially available polymer of Schaap, Thayer, and Valenti.[13]

Experimental Section

Solvents were reagent grade, and were dried and distilled if necessary. Silica gel powder (50–200 mesh) was purchased from J. T. Baker.

Preparation of Silica Gel Bound Rose Bengal. Procedure I. A benzene (100 mL) solution of (3-chloropropyl)trichlorosilane (21 g, 0.1 mol) and absolute ethanol (14 g, 0.3 mol) was treated dropwise with 0.3 mol of triethylamine. After 3 h the reaction mixture was filtered to remove triethylamine hydrochloride, and then it was distilled under reduced pressure to yield 19.2 g of triethoxychlorosilane, bp 156 °C.[14]

Silica gel (10 g), dried at 120 °C for 10 h, was stirred at reflux overnight with triethoxychlorosilane (10 g, 0.41 mol) in *o*-xylene. After the mixture was cooled, the silica gel was filtered and then washed with MeOH, acetone, chloroform, and benzene and furthermore extracted (overnight) in a Soxhlet extractor using MeOH–$CHCl_3$ (2:1). Finally, it was dried at 70 °C for 7 h in a vacuum oven. The resulting silylated silica gel (I) was a white powder similar to the original.

A mixture of the silylated silica gel (4 g) I and rose bengal (2.4 g, 0.5 mol) in 30 mL of DMF was stirred at 135 °C for 17 h. The resulting bright red silica gel was washed with copious quantities of H_2O, MeOH, acetone, $CHCl_3$, and benzene. Further washing in a Soxhlet extractor using MeOH until no more visible color appeared gave a cherry red silica gel which was dried at 50 °C for 10 h in a vacuum oven. The rose bengal loading determined by hydrolysis was 6.6 mg/g. By use of a similar procedure, 4 g of the silylated silica gel and rose bengal (0.8 g, 0.015 mol) afforded an orange-colored silica gel with a loading of 0.65 mg/g as determined by hydrolysis.

Procedure II. Another silica gel rose bengal could be prepared as follows: Silica gel (10 g) was heated in benzene (100 mL) with 15 mL of thionyl chloride for several hours. The chlorinated silica gel resulting was filtered and treated immediately with various concentrations of rose bengal in dimethylformamide. In a typical experiment, rose bengal (2.4 g, 0.005 mol) gave a rose bengal silica gel which had 2.6-mg/g rose bengal. Rose bengal incorporation was measured by hydrolysis as indicated below. These rose bengal polymers were rejected for extensive study, however, because they were rather quickly hydrolyzed when used as photooxidation sensitizers.

2,3-Diphenyl-*p*-dioxene was prepared according to the method of Summerbell and Berger, and the solid thus obtained was recrystallized twice from hexane, mp 93–94 °C (uncorrected).[15]

Photooxidation Procedure. The photooxidation of 200 mg of the 2,3-diphenyldioxene was carried out in 50 mL of solvent in a 3-cm Pyrex tube equipped with a gas inlet tube and a magnetic stirring bar. The entire apparatus was immersed in a water bath maintained at 10 ± 1 °C. Oxygen was constantly bubbled into the solution during the irradiations. The light source was a 500-W tungsten halogen lamp (GEQ 500 T 3 Cl) with a UV cutoff filter (Corning 3060).

Cleavage of $[P_{Si}]$-Rose Bengal. Analysis of the Bound Reagent. In a typical experiment, silica gel bound rose bengal (50 mg) was treated for 1 day with 300 mg of KOH in 40 mL of MeOH with stirring at room temperature. The colorless silica gel was filtered and washed with MeOH to remove all absorbed rose bengal. The filtrate was combined, transferred into a 50-mL volumetric flask, and diluted to 50 mL with MeOH. From the visible spectrum (550 nm) of that solution the amount of free rose bengal was calculated by comparison with the absorption intensity of an authentic rose bengal solution.

Kinetic Method. The rate of photooxidation of the 2,3-diphenyldioxene with $[P_{Si}]$-rose bengal in various solvents was determined as follows: A 50-mL solution (10 ± 1 °C) of the dioxene (200 mg) containing, for example, 200 mg of $[P_{Si}]$-rose bengal was irradiated under O_2 bubbling with the aforementioned visible lamp. Stirring was continued throughout the irradiation. Solution (0.50 mL) was pipetted out at given intervals and diluted to 50 mL (CH_3CN). The decreasing amounts of the dioxene λ_{max} (ϵ 8400 at 306 nm) were monitored as a function of time.

Photoreaction of 2,3-Diphenyldioxene with Polymer-Bound Rose Bengal. General Procedure. To 200 mg of the dioxene in various solvents were added polymer-attached rose bengals. Oxygen was continuously introduced into the solution with constant vigorous stirring. The solutions were irradiated with a 500-W tungsten lamp at 10 °C for 2 h. After evaporation of the solvents below 10 °C, the residue was dissolved in $CHCl_3$ and subjected to NMR analysis (Varian A-60 or Varian CFT-20). The mole ratios of the starting material and products were determined from known spectra of the expected products.[2,3a]

Photooxidation of Tryptophan. Tryptophan (100 mg, 0.0005 mol), $[P_{Si}]$-rose bengal (200 mg, 6.5 mg/g), and 100 mL of distilled water were placed in the photochemical immersion apparatus (described above) and irradiated at 10 °C for 4–6 h in the presence of bubbling oxygen. Tryptophan concentration was monitored by its absorption λ_{max} (ϵ 4900).

Oxidation of Sulfite. The oxidation of sodium sulfite was carried out according to the procedure developed by Srinivasan[11] except that the polymer-based sensitizers [P]-rose bengal and $[P_{Si}]$-rose bengal were substituted for rose bengal.

Acknowledgment. This work was supported by the National Science Foundation. Ms. Liesner gratefully acknowledges a summer research stipend from the Research Corporation.

Registry No. I, 4344-45-0; II, 67592-95-4; III, 94-49-5; (3-chloropropyl)trichlorosilane, 2550-06-3; triethoxy(3-chloropropyl)silane, 5089-70-3; silica gel, 7631-86-9; rose bengal, 11121-48-5; tryptophan, 6912-86-3; sulfite, 14265-45-3; sulfate, 14808-79-8; *N*-formylkynurenine, 1022-31-7.

---

(13) Schaap, A. P.; Thayer, A. L.; Valenti, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4016. Marketed as Sensitox II.

(14) Kaufman, H. C. "Handbook of Organometallic Compounds"; Van Nostrand: Princeton, NJ, 1961; p 333.

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