stantial bathochromic shift in the emission maximum. Consequently, *both* the LF and MLCT states have been energetically lowered with the result that their energy difference is not varied dramatically by the substitution of **4** for bpy.

Additionally, $Ru(1)_3^{2+}$ has been prepared, and, again, its spectroscopic properties have been investigated. The absorption spectra for both $Ru(bpy)_3^{2+}$ and $Ru(1)_3^{2+}$ are shown in Figure 5. There is a small bathochromic shift ($\sim$600 cm^{-1}) in the absorption band assigned to the MLCT transition. Again, this indicates that MLCT states are not substantially affected by substitution of **1** for bpy. In contrast to the previous complexes, this complex did not emit at 298 K. In fact, only a very weak emission was observed even at 77 K. This weak emission displayed none of the fine structure apparent in **2** and **3**. Consequently, we suggest that this polypyridine ruthenium(II) complex has the lowest excited state characterized by mainly a LF configuration. Taking into account the small bathochromic shift in the MLCT state, these results suggest that the LF state's energy has been reduced by approximately 3000 cm^{-1}. On the basis of the results for the Ni(II) complexes, this seems a very reasonable estimate.

In summary, the 4,5-diazafluorene ligand permits the selective perturbation of LF states. The application of this approach to polypyridine ruthenium complexes leads to the conclusion that the MLCT and LF states are in thermal equilibrium. This approach will surely assist in the assignment and "fine tuning" of the excited states in other polypyridine complexes.

Novel Rose Bengal Derivatives: Synthesis and Quantum Yield Studies

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Abstract: The synthesis of several rose bengal derivatives soluble in nonpolar solvents is described. The bis(triethylammonium salt) of rose bengal, **2**, and the triethylammonium salt of the benzyl and ethyl esters of rose bengal, **10** and **11**, are soluble in methylene chloride and chloroform (Scheme I). The tributylammonium salt of the octyl ester of rose bengal, **12**, is also soluble in toluene. The quantum yields of singlet oxygen formation in methanol are equal to, or approaching, that of the disodium salt of rose bengal, **1** (Table VI). The derivatives also show good quantum yields in nonpolar solvents although they are somewhat lower in these solvents than they are in methanol. Electronic absorption spectroscopy points to dye association and equilibration between the quinoid and the lactonic forms or between solvent separated and tight ion pair of the dyes as possible reasons for the lower quantum yields in nonpolar solvents.

Rose bengal (3',4',5',6'-tetrachloro-2'-(2,4,5,7-tetraiodo-6-hydroxy-3-oxo-3*H*-xanthen-9-yl)benzoic acid, bis(sodium salt)) is one of the most efficient and most used singlet oxygen sensitizers (Table I). Though this sensitizer is very useful in polar solvents, it is essentially insoluble in typical organic solvents such as pentane and methylene chloride, and in these solvents effectively no singlet oxygen is formed. Rose bengal, commercially available as the disodium salt, has a major disadvantage in applications in which either the polar solvent reacts with the products of singlet oxygenation or the reagent reacts with or is insoluble in the polar medium. One solution to the problem was that reported "by our group and Schaap's" over 10 years ago; in that instance we immobilized rose bengal via the C-2' carboxylate center to lightly cross-linked polystyrene beads.[1-3] This polymer-based rose bengal system is made compatible with most nonpolar solvents by virtue of the nonpolar polystyrene backbone, and the polymer serves as a vehicle to carry the polar sensitizer into the proximity of reagents dissolved in a nonpolar solvent. There are several limitations of polymer rose bengal, however. One of the more important is that

its quantum yield of singlet oxygen formation is about one-half that of rose bengal "dissolved in poor solvents". Rose bengal may also be solubilized in nonpolar solvents by the addition of crown ethers,[4-7] but under these conditions one still faces the several problems indigenous to rose bengal itself.[2,3] Among the most important and major disadvantages of commercial rose bengal is impurity. Samples obtained from commercial manufacturers are rarely more than 90% rose bengal. The samples always contain inorganic impurities, and sometimes other polyhalogenated uranine salts contaminate the samples (see Experimental Section). Chromatographic purification of the sensitizer is largely ineffective, and the rose bengal samples obtained after even the most elaborate of these purification schemes[8,9] are generally no more pure than was the original commercial sample. Also the quantities of purified material obtained chromatographically are very minimal. Thus, physical measurements made with and synthetic processes carried

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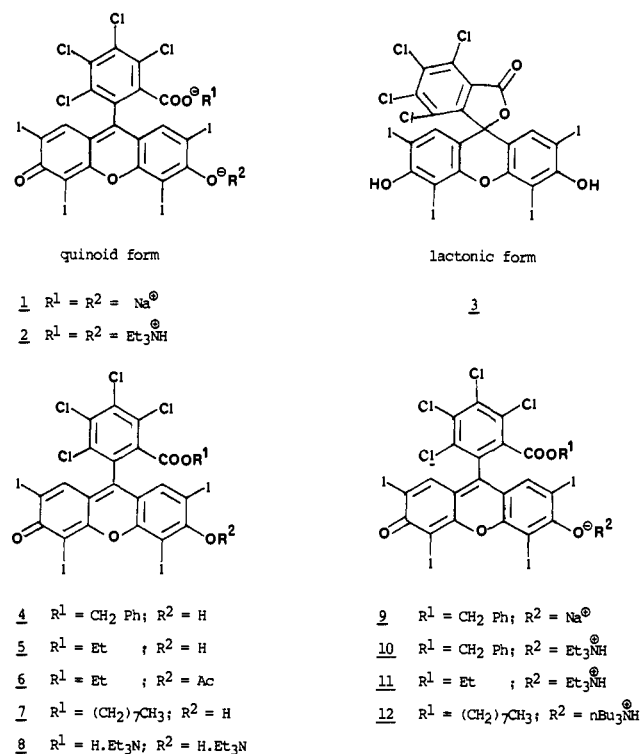
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Table I. Singlet Oxygen Sensitizers (Solubility, Electronic Absorption Maximum (λ_{max}), Molar Absorptivity (ϵ), and Quantum Yield of Singlet Oxygen Formation (Φ_{1O_2}))
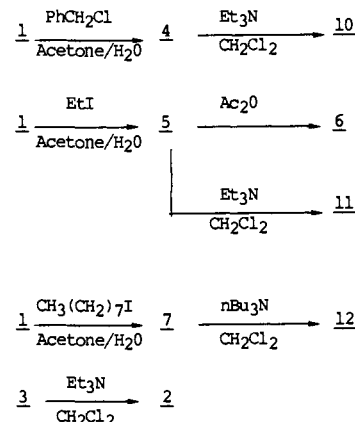
	solubility					
sensitizer	MeOH	CH_2Cl_2	benzene	λ_{max}, nm	ϵ	Φ_{1O_2}
rose bengal[a]	+	−	−	558 (MeOH)	104 700	0.76
erythrosin[a]	+	−	−	530 (MeOH)	94 000	0.62
methylene blue	+	+	−	665 (EtOH)	89 000	>0.23[d]
chlorophyll a[b]	+		+	666 (MeOH)	66 000	>0.77[d]
hematoporphyrin	+		+	529 (EtOH)	316	
zinc tetraphenylporphine[c]	−		+	595 (EtOH)	7 000	
				555 (EtOH)	22 000	

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Scheme I. Structure of the Rose Bengal Derivatives

Scheme II. Synthesis of the Rose Bengal Derivatives

photosensitizers are being developed which can be specifically targeted in tumor cell treatment protocols.[11,20]

Accordingly, we began some years back to develop sensitizers based on the rose bengal skeleton which were soluble in nonpolar solvents and to determine which of these were the most effective singlet oxygen sensitizers and in which solvents they could be effectively used. It was our eventual goal to develop a series of structurally related dyes which combined different hydrophilic and hydrophobic properties with a high molar absorbtivity and a high quantum yield of singlet oxygen formation. Among the purposes we anticipated for these compounds was their application in biological systems and in phototherapy since these systems are so microheterogeneous that it is difficult to determine, a priori, what the most important physical and solubility properties might be.

We report herein a (now) simple, large-scale synthesis of highly pure rose bengal derivatives which differ from the parent dye in physical properties but not significantly in photochemical characteristics, which are mutually soluble in both MeOH and methylene chloride or toluene, and which can be obtained pure without the use of chromatography. The influence of the structure of the dye on the quantum yield of singlet oxygen formation, as well as on the spectral properties of the dye, is also described.

Results and Discussion

The syntheses described in Scheme II and in the Experimental Section are based on the marked difference in the nucleophilicity of the carboxylate and the phenolate group of **1**.[21] In these syntheses, it is convenient that the products except **12** are not very soluble in ether, whereas impurities are very soluble and can be washed away easily. As we have described previously, this difference is attributable to both the steric influence of the C-5 and C-7 iodine atoms and the extensive delocalization of charge provided the C-6 phenoxide by the xanthene skeleton of rose bengal. This difference in nucleophilicity turns out to be a major advantage in manipulating the rose bengal skeleton and provides

out with either rose bengal from a bottle labeled rose bengal or from a chromatographically purified sample of the same have likely rarely been carried out with the same photosensitizer.

There are many reasons why efforts should be expended to both develop new photosensitizers based on the rose bengal skeleton and clarify what turns out to be the relatively difficult dye chemistry associated with the 2-(6-hydroxy-3-oxo-3*H*-xanthen-9-yl)benzoic acid skeleton. Photosensitizers are seeing renewed use in photodynamic applications in photomedicine and photobiology.[10-18] Dyes related to rose bengal, the fluoresceins, are extensively used as active site titrants for serine proteases[19] as well as for fluorescent markers in many biological applications, and

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Table II. Visible Absorption Spectra of Rose Bengal Derivatives in Methanol

	R^1	R^2	λ_{max}, nm	ϵ	log ϵ	$\epsilon_1/\epsilon_2{}^a$	solvent concn, M
1	Na	Na	558	104 713	5.02	3.24	MeOH
			528 (min)	11 220	4.47		4.91×10^{-6}
			518	32 359	4.51		
9	PhCH$_2$	Na	564	102 329	5.01	3.24	MeOH
			534 (min)	28 840	4.46		4.81×10^{-6}
			524	31 623	4.50		
2	TEA	TEA^b	557	109 500	5.04	3.19	MeOH
			527 (min)	31 898	4.50		5.53×10^{-6}
			519	34 341	4.54		
11	Et	TEA	563	86 351	4.94	2.89	MeOH
			534 (min)	27 941	4.45		5.58×10^{-6}
			524	29 914	4.48		
10	PhCH$_2$	TEA	563	91 109	4.96	2.96	MeOH
			533 (min)	28 936	4.46		5.02×10^{-6}
			524	30 808	4.49		
12	(CH$_2$)$_7$CH$_3$	TBA^c	564	103 226	5.01	3.13	MeOH
			535 (min)	29 863	4.48		4.33×10^{-6}
			525	32 960	4.52		

$^a \epsilon_1/\epsilon_2$ is the ratio of the molar absorptivities of the largest wavelength absorption maximum (558, 564) and the secondary maximum (518, 524). ^{b} TEA = triethylammonium. ^{c} TBA = tri-n-butylammonium.

Table III. Visible Absorption Spectra of the Rose Bengal Derivatives in Dichloromethane

	R^1	R^2	λ_{max}, nm	ϵ	log ϵ	ϵ_1/ϵ_2	solvent concn, M
2	TEA	TEA	556	76 394	4.88	2.35	CH$_2$Cl$_2$
			539 (min)	28 849	4.46		4.97×10^{-6}
			518	32 568	4.51		
11	Et	TEA	563	73 705	4.87	2.15	CH$_2$Cl$_2$
			537 (min)	30 225	4.48		4.71×10^{-6}
			525	34 254	4.53		
10	PhCH$_2$	TEA	569	61 735	4.79	2.24	CH$_2$Cl$_2$
			541 (min)	24 395	4.39		5.02×10^{-6}
			528	27 582	4.44		

a series of derivatives from rose bengal which would be much more difficult to obtain from other members of the uranine/fluorescein series.

In a previous communication we have described the influence of derivatization of the carboxylate and the phenolate function on the electronic absorption spectrum of the dye.[3] Blocking of the phenolate function shifts the λ_{max} from 558 nm ($\epsilon \simeq 10^5$) to 494 nm ($\epsilon \simeq 10^4$) as illustrated by the synthesis of 6-O-acetyl rose bengal ethyl ester (3',4',5',6'-tetrachloro-2'-(2,4,5,7-tetra-iodo-6-acetyloxy-3-oxo-3H-xanthen-9-yl)benzoic acid ethyl ester (**6**) which is soluble in methylene chloride. Although the quantum yield of singlet oxygen formation from **6** is large enough compared to that of **1** to make it a useful singlet oxygen sensitizer (Table VI), its low molar absorbtivity is a major drawback.

In order to obtain a sensitizer with a high molar absorptivity, the xanthene portion of the system must be preserved as the monoanion (C-6) so that the phenolate salt is needed. For solubility in nonpolar solvents the gegenion must form a tight ion pair, or be soluble in nonpolar solvents itself. The notion that triethylammonium hydrochloride is soluble in methylene chloride and chloroform prompted us to synthesize triethylammonium derivatives of **1**. These were obtained easily from rose bengal lactone **3** or from esters of **1**.

Rose bengal lactone **3** reacts readily with bases so treatment with Et$_3$N immediately yields the bis(triethylammonium) salt **2**, which is in the quinoid form as are all rose bengal salts. The molecular forms of rose bengal esters (**4, 5, 7**) have a very acidic phenolic proton at C(6) and can be converted to their mono-(triethylammonium) salts **10** and **11** or mono(tributylammonium) salt **12** by addition of Et$_3$N or n-Bu$_3$N, respectively. In the process the monoanionic form of the xanthene portion of rose bengal is generated. The solubility of compounds **2** and **10–12** in methylene

chloride and chloroform is excellent. Compound **12**, because of its long alkyl chain, is even soluble in toluene, and it seems that solubility in even less polar solvents might be obtained by introducing even longer chain alkyl groups in the ester portion of the molecule or the ammonium salt.

Elemental Analysis Elemental analysis was performed on two different samples of commercial rose bengal, on rose bengal bis(triethylammonium salt), **2**, and on rose bengal ethyl ester triethylammonium salt, **11** (see Experimental Section). These compounds served as models for the other derivatives. It is evident that the quality of the commercial samples is not consistent and that our derivatives show a marked improvement in comparison. The same improvement is visible in the ratio of the number of equivalents of chlorine and of iodine which is a measure of the absence of inorganic chloride.

Electronic Absorption Spectra in Various Solvents Table II shows the electronic absorption data in the visible region in methanol of the rose bengal derivatives and comparison of the spectra with the disodium salt of rose bengal **1** and the rose bengal benzyl ester sodium salt **9**. As we have previously pointed out, esterification of the carboxylate moiety of rose bengal is accompanied by a shift of the absorption maxima from 558 to 564 nm and from 518 to 524 nm, respectively.

The electronic absorption data in dichloromethane are shown in Table III. The most noticeable features in comparison with Table II are the lower ϵ values for the longest wavelength absorption maximum and for the ratio ϵ_1/ϵ_2. The latter is the ratio of the extinction coefficient of the two wavelength maxima. Both effects are even more pronounced in Table IV which shows the data for the rose bengal octyl ester tributylammonium salt **12** in toluene. In this case and for **10** in dichloromethane there is also a shift of the secondary absorption maximum compared to MeOH

Table IV. Visible Absorption Spectrum of Rose Bengal Octyl Ester Tributylammonium Salt in Toluene

	R^1	R^2	λ_{max}, nm	ϵ	log ϵ	ϵ_1/ϵ_2	solvent, concn, M
12	$(CH_2)_7CH_3$	TBA	563	49 406	4.69	0.86	toluene
			549 (min)	32 471	4.51		4.64×10^{-6}
			536	57 529	4.76		

Table V. Effect of Addition of Triethylamine to Solutions of **2** and **10** in CH_2Cl_2

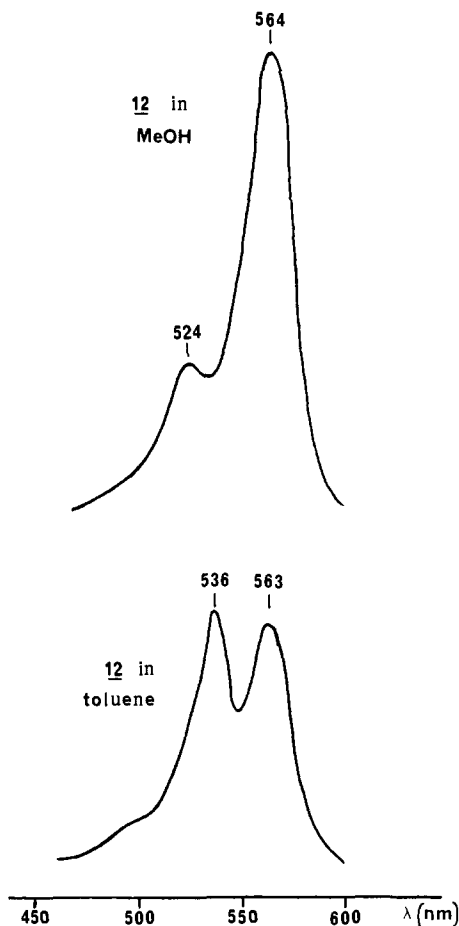|	R^1	R^2	λ_{max}, nm	ϵ	log ϵ	ϵ_1/ϵ_2	solvent
2	TEA	TEA	564	123 034	5.090	3.62	CH_2Cl_2
			534 (min)	29 311	4.467		
			523	34 015	4.532		
10	$PhCH_2$	TEA	572	99 573	4.998	3.23	CH_2Cl_2
			542 (min)	27 183	4.434		
			530	30 868	4.490		

Figure 1. Electronic absorption spectrum of **12** in methanol and toluene.

from 525 to 536 nm and from 524 to 528 nm, respectively. The completely different shapes of the spectra of **12** in toluene and in methanol are shown in Figure 1 for reference. We suggest these data indicate association of dye molecules in more nonpolar solvents, and spectra taken at higher concentrations of dye show a decrease in the ϵ_1/ϵ_2 ratio.

From the measurement of quantitative electronic absorption spectra we also have an indication that an equilibrium between the quinoid and lactonoid form of the dye and/or tight ion pairs and solvent-separated ion pairs may be involved (Scheme III). An illustration of this is the data in Table V. In Table V we show the effect of adding a small amount of triethylamine to the corresponding solutions in Table III. It is evident that there is a dramatic increase in the molar absorptivity of the largest wavelength absorption band as well as of the ϵ_1/ϵ_2 ratio. In addition we observe a slight shift to longer wavelengths.

Quantum Yields of Singlet Oxygen Formation of the Rose Bengal Derivatives. The quantum yields of singlet oxygen formation of

Scheme III. Equilibration between the Quinoid and Lactonic Forms of **2** in CH_2Cl_2

$$\underline{2} \; \rightleftharpoons \; \underline{8} \; \rightleftharpoons \; \underline{3} + 2 \; Et_3N$$
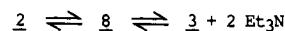
Scheme IV. The Photooxygenation of 2,3-Diphenyl-p-dioxene (13)

$\underline{13}(A)$ $\underline{14}$ $\underline{15}(AO_2)$
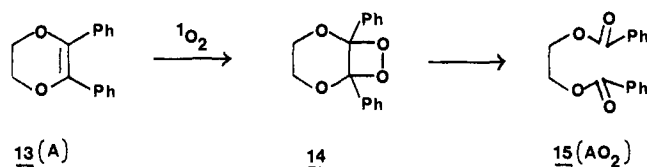
Scheme V. Reaction of Singlet Oxygen Produced by Rose Bengal (RB) with 2,3-Diphenyl-p-dioxene (A)

$$RB \xrightarrow{\;h\nu\;} {}^1RB* \tag{1}$$

$$^1RB \xrightarrow{\;k_2\;} {}^3RB* \tag{2}$$

$$^3RB* + O_2 \xrightarrow{\;k_3\;} {}^1O_2 + RB \tag{3}$$

$$^1O_2 \xrightarrow{\;k_4\;} O_2 \tag{4}$$

$$^1O_2 + A \xrightarrow{\;k_5\;} AO_2 \tag{5}$$

$$v_{AO_2} = I_{abs} \times \Phi_{{}^1O_2} \times \phi_{AO_2} \tag{6}$$

$$\phi_{AO_2} = \frac{k_5[A]\,[{}^1O_2]}{k_5[A]\,[{}^1O_2] + k_4[{}^1O_2]} = 1 \; \text{if} \; k_4[{}^1O_2] \ll k_5[A][{}^1O_2] \tag{7}$$

$$\frac{(v_{AO_2})_{RB}}{(v_{AO_2})_{\underline{1}}} = \frac{(I_{abs})_{RB}(\Phi_{{}^1O_2})_{RB}(\phi_{AO_2})_{RB}}{(I_{abs})_{\underline{1}}\;(\Phi_{{}^1O_2})_{\underline{1}}\;(\phi_{AO_2})_{\underline{1}}} = \frac{(\Phi_{{}^1O_2})_{RB}}{(\Phi_{{}^1O_2})_{\underline{1}}} \tag{8}$$

$$(v_{AO_2})_{RB} = (v_{AO_2})_{\underline{1}}\frac{(\Phi_{{}^1O_2})_{RB}}{(\Phi_{{}^1O_2})_{\underline{1}}} = (v_{AO_2})_{\underline{1}}\frac{(\Phi_{{}^1O_2})_{RB}}{0.76} \tag{9}$$

I_{abs} = rate of light absorption.

ϕ_{AO_2} = quantum efficiency for AO_2 formation.

AO_2 = ethylene glycol dibenzoate $\underline{15}$.

the rose bengal derivatives in different solvents were obtained by using the relative actinometric method developed by Schaap and Thayer.[1] The rate of photooxidation of 2,3-diphenyl-p-dioxene (**13**) is compared for **1** and the rose bengal derivative in question

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Table VI. Quantum Yields of Singlet Oxygen Formation

compd	R^1	R^2	$\Phi_{^1O_2}$	solvent
1	Na	Na	0.76^a	MeOH
5	Et	H	0.73	MeOH
2	TEA^b	TEA	0.72	MeOH
10	PhCH$_2$	TEA	0.74	MeOH
11	Et	TEA	0.74	MeOH
2	TEA	TEA	0.48	CH$_2$Cl$_2$
10	PhCH$_2$	TEA	0.67	CH$_2$Cl$_2$
11	Et	TEA	0.71	CH$_2$Cl$_2$
5	Et	H	0.61	CH$_2$Cl$_2$
6	Et	Ac	0.61	CH$_2$Cl$_2$
12	(CH$_2$)$_7$CH$_3$	TBA^c	0.40	PhCH$_3$

^{a}Gollnick, K.; Schenck, G. O. *Pure Appl. Chem.* **1964**, *9*, 507. ^{b}TEA = triethylammonium. ^{c}TBA = tributylammonium.

(RB) (Schemes IV and V). The concentration of the dye is so high that all of the light is abosrbed, $(I_{abs})_1 \simeq (I_{abs})_{RB}$, and the reactivity of **13** is such that the rate of its oxidation is greater than the rate of physical quenching of singlet oxygen by the solvent, $k_5[A][^1O_2] \gg k_4[^1O_2]$. Essentially every dye molecule in the T$_1$ state leads to a molecule of the oxidation product of **13**, ethylene glycol dibenzoate **15**. Under these conditions the quantum yield of singlet oxygen formation can be derived from eq 9 in which $(v_{AO_2})_{RB}$ and $(v_{AO_2})_1$ are the rates of formation of **15** for the dye RB and **1**, respectively. $(\Phi_{^1O_2})_{RB}$ is the quantum yield for dye RB, and 0.76 is the yield for **1**.[22,23]

Table VI shows the quantum yields of singlet oxygen formation for the new rose bengal derivatives. In MeOH the quantum yields for all of the new derivatives are the same as that of **1** within the margin of experimental error. In methylene chloride and toluene, the values average somewhat lower than 0.76 possibly due to some singlet oxygen quenching from release of triethylamine into solution by equilibration with the lactonic form (Scheme III). Also, if incomplete transfer of the acidic hydrogen atoms of the dye to the triethylamine occurs, the lone pair of the nitrogen atom of the amine is available for electron transfer to the singlet oxygen and consequently for quenching.[24] There is evidence for this in the lower molar absorptivity in the electronic absorption spectra of the dyes in dichloromethane and toluene. Also the results show the absence of any solvent effect as the lifetime of singlet oxygen in dichloromethane (140 μs) is considerably longer than in methanol (11 μs) whereas the quantum yields in dichloromethane are lower than in methanol.[25]

The results show that it is possible to convert the disodium salt of rose bengal **1** to highly pure ammonium salts soluble in a variety of nonpolar solvents through a simple synthetic procedure. The new dyes have good molar absorptivity in the same region as **1** itself and a high quantum yield of singlet oxygen formation. Derivatization of the 2′-carboxylate group has no negative effect on the sensitizing ability of the dye. Since rose bengal is the only dye with a substituent which can be easily manipulated chemically without fundamentally affecting the photophysical properties of the dye, this opens up new opportunities for designed dye derivatives for specific applications.

Experimental Section

General. Rose bengal **1**, dye content 92%, was purchased from Aldrich. ^{1}H NMR spectra were measured on a Varian CFT-20 79.6-MHZ ^{1}H NMR spectrometer in CDCl$_3$ with Me$_4$Si as internal standard. Chemical shifts are reported in δ and *J* values in Hz. Infrared spectra were obtained with a Perkin-Elmer 337 grating IR spectrometer and electronic absorption spectra with a Varian Cary 219 instrument. Quantum yields were measured with a Bausch and Lomb high-intensity

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(23) Gandin. E.; Lion, Y.; Van de Vorst, A. *Photochem. Photobiol.* **1983**, *37*, 271.
(24) For a discussion of quenching mechanisms of singlet oxygen by amines, see: Foote, C. S. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 157–159 and references therein.
(25) Young, R. H.; Brewer, D. R. In "Singlet Oxygen"; Rånby, B., Rabek, J. F., Eds.; Wiley: Chichester, 1978; p 40.

monochromator fitted with an Osram HBO 200W-L2 super-pressure mercury lamp. GLC analysis was performed on a Hewlett-Packard gas chromatograph fitted with a glass capillary column (i.d. 0.20 mm, length 12 m) containing a cross-linked methyl silicone film (film thickness 0.33 μm) and a flame ionization detector. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthetic Procedures. The syntheses of rose bengal benzyl and ethyl ester, **4** and **5**, and of rose bengal lactone **3** and 6-*O*-acetyl rose bengal ethyl ester **6** have been described in a previous publication.[2]

Rose Bengal Bis(triethylammonium Salt) (2). Rose bengal lactone **3**, formed by acid precipitation of the commercial product from an aqueous solution, was suspended in CH$_2$Cl$_2$ and treated with excess Et$_3$N. This yielded a clear red solution which was evaporated in vacuo. The resulting purple-red powder was placed on a filter, thoroughly washed with Et$_2$O to remove residual Et$_3$N, and finally dried in a vacuum oven at 80 °C. Isolated yield of **2** is 80%.

^{1}H NMR (CDCl$_3$) δ 1.18 (t, amine-CH$_3$, 18 H), 2.98 (q, –CH$_2$-N, 12 H), 7.57 (s, xanthene-H, 2 H).

Elemental Anal. Calcd: C, 32.68; H, 2.91; Cl, 12 06; I, 43.16. Found: C, 32.72; H, 3.00; Cl, 11.92; I, 42.96. Equiv Cl/equiv I = 0.99.

Commercial rose bengal disodium salt **1**. Calcd: C, 23.61; H, 0.20; Cl, 13.94;, I, 49.88. Sample 1: Found: C, 21.69; H, 0.91; Cl, 14.11; I, 46.52. Sample 2: Found: C, 22.45; H, 0.90; Cl, 15.12; I, 44.11. Equiv Cl/equiv I = 1.09 and 1.23, respectively.

Rose Bengal Benzyl Ester Triethylammonium Salt 10. Rose bengal benzyl ester molecular form **4** was dissolved in CH$_2$Cl$_2$ yielding an orange solution. Upon addition of excess Et$_3$N, the solution turned deep red and was evaporated in vacuo. The resulting purple-red powder was thoroughly washed with Et$_2$O to remove residual Et$_3$N and dried in a vacuum oven at 80 °C. Isolated yield of **10** is 80%.

^{1}H NMR (CDCl$_3$) δ 1.33 (t, amine-CH$_3$, 9 H), 3.10 (q, CH$_2$-N, 6 H), 4.97 (s, benzyl-CH$_2$, 2 H), 6.9-7.5 (m, Ar-H, 5 H), 7.29 (s, xanthene-H, 2 H). IR (KBr) 1730 cm^{-1} (ester C=O).

Rose bengal ethyl ester triethylammonium salt **11** was synthesized from rose bengal ethyl ester, molecular form **5**, in complete analogy to **10** from **4**.

^{1}H NMR (CDCl$_3$) δ 0.92 (t, ester-CH$_3$, 3 H), 1.38 (t, amine-CH$_3$, 9 H), 3.18 (q, CH$_2$-N, 6 H), 4.00 (q, ester-CH$_2$, 2 H), 7.40 (s, xanthene-H, 2 H). IR (KBr) 1730 cm^{-1} (ester C=O).

Elemental Anal. Calcd: C, 30.49; H, 2.10; Cl, 12.86; I, 46.02. Found: C, 30.28; H, 2.17; Cl, 12.69; I, 45.77. Equiv Cl/equiv I = 0.99.

Rose Bengal Octyl Ester Tri-*n*-butylammonium Salt 12. Rose bengal octyl ester molecular form **7** was synthesized by refluxing **1** in acetone/water (1:1) with 5 equiv of 1-iodooctane analogous to the syntheses of **4** and **5**. The ester **7** was converted to **12** by addition of excess *n*-Bu$_3$N to a solution of **7** in CH$_2$Cl$_2$, evaporating to dryness, and washing with hexane. Isolated yield of **12** is 80%.

^{1}H NMR (CDCl$_3$) δ 0.5-2.3 (m, alkyl-H of octyl and butyl groups, 36 H), 3.1 (t, CH$_2$-N, 6 H), 3.9 (t, CH$_2$-O, 2 H), 7.45 (s, xanthene-H, 1 H). IR (KBr) 1730 cm^{-1} (ester C=O).

Quantum Yield Measurement of Singlet Oxygen Formation. A solution (5 mL) of 2,3-diphenyl-*p*-dioxene (**13**) (2.9 × 10^{-2} M) and the dyes **2** or **10–12** (2.7 × 10^{-4} M) in a Pyrex cell was irradiated in a high-intensity monochromator with 561-nm light. The calculated absorbance of such a solution at 561 nm is 5 – 27, depending on the ϵ at the λ_{irr} = 561 nm so that all the light is absorbed. The solution was stirred and a continuous flow of oxygen over the surface of the solution was maintained throughout the experiment. The formation of the photooxygenation product ethylene glycol dibenzoate **15** was followed by analysis of aliquots of the solution by GLC at 235 °C at regular intervals. $\Phi_{^1O_2}$ was calculated from the ratio of the rate of formation of **15** for a dye compared to the rate for rose bengal **1** and the known quantum yield for **1** ($\Phi_{^1O_2}$ = 0.76) according to eq 9 (Scheme V).[23,24]

The quantum yield of $^1O_2$ formation of **5** and **6** in CH$_2$Cl$_2$ was measured by irradiation with 500-nm light on a solution 2.9 × 10^{-3} M in **13** and 5.4 × 10^{-4} M in the dye. The calculated absorbance of such a solution is around 5.4 at 500 nm so that all the light is absorbed. The rates of formation of **15** were compared with that of a solution of rose bengal **1** of the same composition which also has an absorbance of around 5.4 at 500 nm.