2 h. The solution was evaporated to dryness and extracted with chloroform, and the extract was washed with water and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was recrystallized from ethanol to give white crystals of **18**, 90 mg (30% yield): mp 200 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 4.38 (s, 4 H), 7.20 (s, 8 H); MS, m/z (rel intensity) 294.1363 (91, M^+), calcd 294.1368; IR ν_{max} 1335, 1429, 1466, 1515, 1658 cm^{-1}.

(b) A suspension of 42 mg (1 mmol) of cyanamide in tetrahydrofuran at -60 °C was treated with 650 μL of a 1.6 M solution of *n*-butyllithium. After 30 min a solution of 228 mg (1 mmol) of **19** in 3 mL of tetrahydrofuran was added and the mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo, water was added, and the resulting solid was collected and purified by recrystallization from isopropyl alcohol to give pure **18**, 50 mg (34% yield).

***N*-(Cyanoguanidineacetyl)-*p*-toluidine (20).** (a) A solution of 76 mg of sodium reacted (3.3 mmol) in 5 mL of absolute ethanol was treated with 252 mg (6 mmol) of cyanamide followed by 684 mg (3 mmol) of **19**, and the mixture was stirred at room temperature. During this process **20** (360 mg) precipitated as a white solid and was collected and purified by recrystallization from isopropyl alcohol or ethylene dichloride and purified by recrystallization from isopropyl alcohol or ethylene dichloride to give pure **20**, 350 mg (50% yield): mp 205 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 2.25 (s, 3 H, CH_3), 4.11 (s, 2 H, CH_2), 6.10 (s, 2 H, exchangeable NH), 9.72 (s, 1 H, NHCO); MS, m/z (rel intensity) 231.1121 (6.8, M^+), calcd 231.1120; 189.0902 (2.04, M – H_2NCN), calcd 189.0902; 132.0685 (100, M – $COCH_2NHC{=}NHNH$), calcd 132.0687; IR ν_{max} (Nujol) 1398, 1463, 1606, 1660, 1712, 3210 cm^{-1}.

(b) A solution of 44.6 mg (0.2 mmol) of **21** in 2 mL of methanol was treated with a solution of 70 mg (0.22 mmol) of mercuric acetate in 1 mL of methanol. The mixture turned deep red and then black and HgS precipitated. The precipitate was collected and the filtrate evaporated to dryness, water was added, and the solution was extracted with methylene chloride. The solvent was removed in vacuo and the residue dissolved in ethanol and then allowed to react with cyanamide in the presence of sodium ethoxide to give **23**, 30 mg (65% yield). TLC (silica gel, methanol/chloroform, 1:9): R_f **21** = 0.45, for **24** R_f 0.5.

Acknowledgment. This investigation was supported by grants (to J.W.L.) from the National Cancer Institute of Canada and the Biotechnology Strategic Grants Programme of the Natural Sciences and Engineering Research Council of Canada.

Registry No. **1**, 616-47-7; **2**, 30148-21-1; **3**, 109012-22-8; **4**, 1564-49-4; **5**, 109012-23-9; **6**, 109012-24-0; **6** (acid chloride), 109012-46-6; **7**, 109012-25-1; **8**, 109012-26-2; **9a**, 109012-27-3; **9b**, 109012-47-7; **9c**, 109012-48-8; **10a**, 109012-28-4; **10b**, 109012-49-9; **10c**, 109012-50-2; **11**, 109012-29-5; **12**, 109012-30-8; **13**, 109012-31-9; **13** (*N*-acetyl derivative), 109012-51-3; **14**, 109012-32-0; **15**, 104394-08-3; **16**, 104394-09-4; **17**, 16634-82-5; **18**, 21303-69-5; **19**, 5343-65-7; **20**, 109012-33-1; **21**, 109012-34-2; **23**, 109012-35-3; **24**, 109012-36-4; **25**, 109012-37-5; **26**, 109012-38-6; **27**, 109012-39-7; **27A**, 109012-53-5; **28**, 101772-43-4; **28A**, 109012-54-6; **29**, 104394-13-0; **29A**, 101772-44-5; **30**, 3185-95-3; **32**, 109012-40-0; **33**, 109012-41-1; **34**, 109012-42-2; **35**, 109012-43-3; **36**, 109012-44-4; **37**, 109012-45-5; **38**, 101809-75-0; **38A**, 104394-05-0; **39**, 104394-12-9; **39A**, 101772-41-2; EtOCOCl, 541-41-3; $H_2NCH_2CH_2CN$, 151-18-8; $ClCH_2COCl$, 79-04-9; $BrCH_2COCl$, 22118-09-8; guanidineacetic acid hydrochloride, 14901-20-3; 3-(1-methyl-4-aminopyrrole-2-carboxamido)propionitrile, 97950-77-1; 1-methyl-4-nitropyrrole-2-carboxylic acid, 13138-78-8; 1-methyl-4-nitropyrrole-2-carboxylic acid chloride, 28494-51-1; *p*-toluidine, 106-49-0; thioureidoacetic acid, 51675-47-9.

Rose Bengal Functionalized Phase-Transfer Catalysts Promoting Photooxidations with Singlet Oxygen. Nucleophilic Displacements on Dioxetanic and Endoperoxidic Intermediates

Alessandro Guarini and Pietro Tundo*†

Istituto di Chimica Organica dell'Università di Torino, Torino, Italy

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Photooxidations with $^1O_2$ promoted by an anionic photosensitizer, such as Rose Bengal, can be readily performed in an aqueous–organic, two-phase system in the presence of catalytic amounts of quaternary onium salts that transfer the anion in the organic phase. This means that one can use low-polar solvents, which are unusual in reactions with this sensitizer. Soluble and silica gel immobilized onium salts were used as the phase-transfer catalysts. If a nucleophile is also present in the reaction mixture, it, too, is transported in the organic phase and reacts via S_N2, if the intermediate is of the dioxetanic or endoperoxidic type. With the heterogenized catalysts it is possible to carry out the reaction in two steps: the photooxidation itself and later the nucleophilic displacement. In addition to being productive with regard to the synthesis, this can clarify the photooxidation reaction pathway. The following organic substrates were photooxidized under PTC conditions: anthracene, 2,3-dimethyl-2-butene, 5,6-dihydro-2,3-diphenyl-*p*-dioxin, 1,3-cyclohexadiene, and indene. In the presence of N_3^- as nucleophile, anthracene gives 10-imino-9(10*H*)-anthracenone while 5,6-dihydro-2,3-diphenyl-*p*-dioxin yields, selectively, two different azido derivatives according to the procedure employed.

Introduction

Singlet oxygen ($^1O_2$) can be generated in various ways, the most important being reaction of $^3O_2$ with the excited state of a photosensitizer: light irradiation of the sensitizer in a solvent in the presence of $^3O_2$ has been reported to produce the oxidation of various substrates.[1]

One of the principal sensitizers is Rose Bengal (3,4,5,6-tetrachloro-2-(2,4,5,7-tetraiodo-6-hydroxy-3-oxo-3*H*-xanthen-9-yl)benzoic acid, disodium salt).[2]

Since Rose Bengal is a disodic salt (Na_2RB) it can only be dissolved in water and strongly polar solvents. It is thus of limited utility in organic synthesis. In addition, on account of its low solubility, Na_2RB forms aggregates in low polar organic solvents with reduced catalytic activity, owing to the formation of excimers.[3] The activity of RB^{2-}

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† Present address: Facoltà di Scienze M.F.N. dell'Università di Messina, Piazza Pugliatti, Messina, Italy.

(1) (a) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395–427. (b) Frimer, A. A. *Singlet O_2*; CRC: Boca Raton, FL, 1984.

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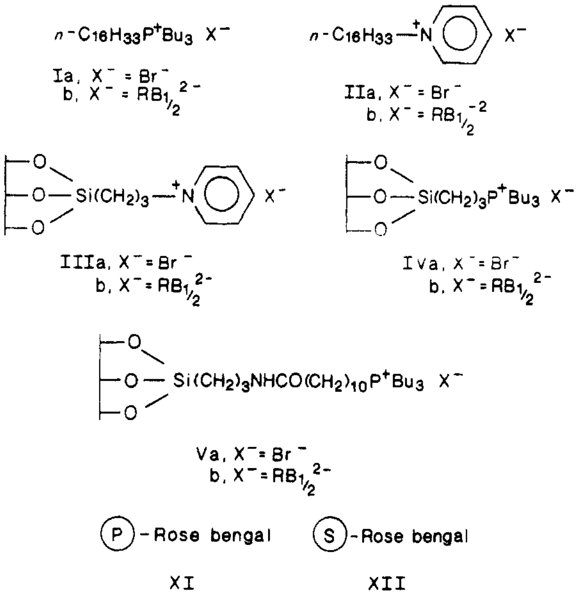
Chart I



remains sufficiently high, however, if a complexing agent (18-crown-6)[4] or an anion transferer (tricaprylmethylammonium chloride, Aliquat 336)[4a] is used in these solvents. The conditions described in the literature in this connection are those of solid–liquid phase-transfer catalysis (SL-PTC).

Moreover, several lipophilic derivatives of Rose Bengal have been prepared to render it more soluble.[5]

Rose Bengal has also been rendered highly active through physical separation of its molecules by chemical immobilization on cross-linked polystyrene[6] or silica gel:[7] low Rose Bengal functionalization on these two supports avoids excimer formation and gives the advantage derived from its immobilization: easy elimination from the reaction mixture, reuse of the catalyst, and cleanup of the reaction.

In this paper, we show that photooxidation reactions with singlet oxygen can be more easily performed in an aqueous–organic two-phase system. RB^{2-}, present in the aqueous phase, is transferred in the organic phase through an anionic exchange reaction promoted by the presence of a lipophilic quaternary onium salt, this being a classic promoter of PTC.[8] PT catalysts have also been immobilized on an organic or inorganic matrix, i.e. cross-linked polystyrene,[9] or silica gel or alumina[10] respectively. Accordingly, it will be shown here that good results can also be obtained when the RB^{2-} is the counteranion of an onium cation chemically bound on a solid silica gel support.

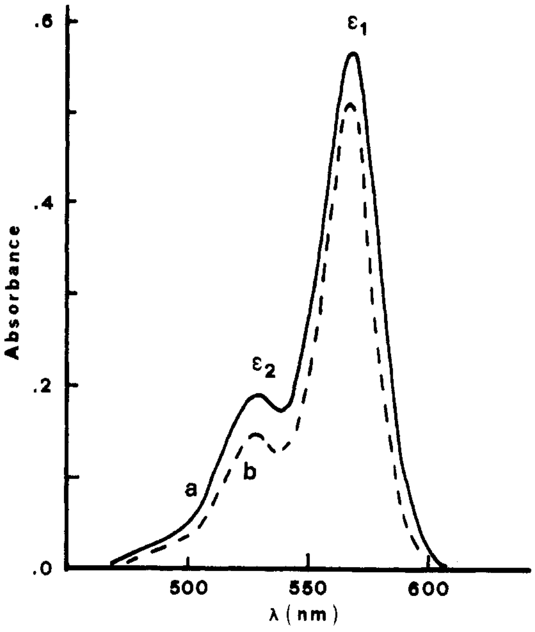


Figure 1. Visible spectra of 5×10^{-6} N solutions of Ib in toluene (a, –) and chloroform (b, - - -). ϵ_1/ϵ_2 (the ratio between the molar absorbivities at λ_1 (562 nm) and λ_2 (523 nm) is 2.81 in toluene and 3.60 in chloroform.

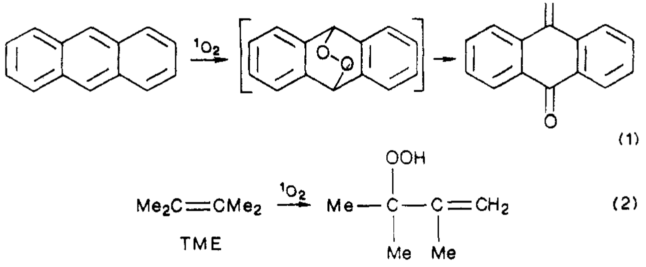
Generally speaking, PTC is an organic synthetic technique which enhances the reactivity of the anion that the lipophilic onium salt brings with it into the organic phase. This enhanced reactivity is due to the decreased interaction between the anion and the solvent. Accordingly, nucleophilic displacement reactions under PTC conditions can indeed take place whenever the first adduct the organic substrate forms with $^1O_2$ is of the dioxetanic or endoperoxidic type and sufficiently stable.

Results

The onium salts used as soluble PT catalysts in this study were commercially available hexadecyltributylphosphonium bromide (Ia) and hexadecylpyridinium bromide (IIa). The onium salts immobilized on silica gel employed (IIIa), IVa, and Va) were obtained as described elsewhere.[10] These systems are shown in Chart I.

The photooxidations were carried out in the apparatus described in the Experimental Section. It was also employed to perform reactions reported by other authors in order to provide a set of comparable results.

Oxidation with $^1O_2$ by means of RB^{2-} in an Aqueous–Organic Two-Phase System Containing a Lipophilic Onium Salt. 18-Crown-6 and Aliquat 336 have already been used to oxidate anthracene to 9,10-epidioxyanthracene and 2,3-dimethyl-2-butene (TME) to the allyl hydroperoxide VI (eq 1 and 2).



(1)

$$Me_2C{=}CMe_2 \xrightarrow{^1O_2} Me{-}\underset{Me}{\overset{OOH}{C}}{-}\underset{Me}{C}{=}CH_2 \qquad (2)$$

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(3) (a) Stevens, B. *Annu. Rep. Prog. Chem., Sect. A: Gen., Phys. Inorg. Chem.* **1974**, *71*, 29–47. (b) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80–86.

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(8) (a) Starks, M.; Liotta, C. *Phase Transfer Catalysis*; Academic: New York, 1978. (b) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147. (c) Dehmlov, E. V.; Dehmlov, S. S. *Phase Transfer Catalysis*, 2nd ed.; Verlag Chemie: Weinheim, 1983.

(9) (a) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421. (b) Anelli, P. L.; Czech, B.; Montanari, F.; Quici, S. *J. Am. Chem. Soc.* **1984**, *106*, 861–869 and references therein. (c) Paczkowska, B.; Paczkowski, J.; Neckers, D. C. *Macromolecules* **1986**, *19*, 863–870.

(10) (a) Tundo, P.; Venturello, P. *J. Am. Chem. Soc.* **1979**, *101*, 6606–6613. (b) Tundo, P.; Venturello, P. *J. Am. Chem. Soc.* **1981**, *103*, 856–861. (c) Tundo, P.; Venturello, P.; Angeletti, E. *J. Am. Chem. Soc.* **1982**, *104*, 6551.

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Table I. Efficiency of Various Systems in the Photooxidation of 5,6-Dihydro-2,3-diphenyl-*p*-dioxin (VII, eq 3)

entry	system	% conversn[b]
1	n-$C_{16}H_{33}P^+Bu_3Br^-$[c]/$CHCl_3$	96
2	30% aqueous acetone[d]	88
3	18-crown-6[c]/$CHCl_3$[e]	88
4	10% aqueous methanol[f]	60

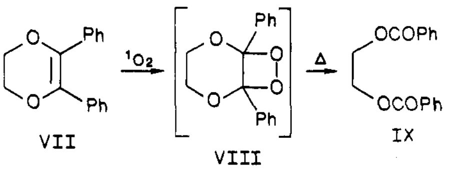
[a] Carried out at 26 °C with 0.01 molar equiv of Na_2RB. VII, 50 mg; solvent, 10.0 mL. For entry 1, H_2O, 2.0 mL. [b] After 8 min. Determined by GLC (under analysis conditions, VIII completely decomposes into IX). [c] 0.02 molar equiv. [d] Conditions of ref 11. [e] Conditions of ref 4. [f] Conditions of ref 11 and 12.

In these studies,[4] a great excess of the transfer agent was used (4–5 molar equiv with regard to the sensitizer).

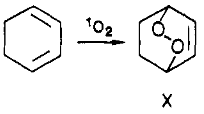
When an aqueous–organic two-phase system is used without a phase-transfer catalyst, no photooxidation takes place, because RB^{2-} is only present in the aqueous phase (compare footnote *b*, Table II). When 2.0 molar equiv of a lipophilic quaternary onium salt is added on the other hand, the purple color appears only in the organic phase.

The visible spectra shown in Figure 1 were obtained under these conditions using 2.0 molar equiv of Ia by quantitatively transferring RB^{2-} from an aqueous phase to an organic one. They are recorded in order to observe the possible presence of ionized ion pairs.

Light irradiation of such a two-phase mixture in the presence of $^3O_2$ is productive, as shown by some typical photooxidation reactions (eq 1–4).



(3)



(4)

Reaction 3 was carried out under both double-phase conditions and the homogeneous conditions reported in the literature. The results (Table I) indicate that the reaction rate is comparable with and higher than those already obtained with the homogeneous systems.

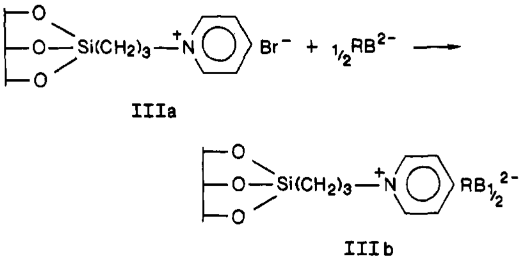
The photooxidation reaction rate of VII in the H_2O–$CHCl_3$ two-phase system, catalyzed by Ib follows zero-order kinetics (see Experimental Section) as already observed in homogeneous conditions.[5] Working at 26 °C, the reaction products are both the intermediate dioxetane VIII and diester IX in approximately equal amounts (TLC on silica gel; eluent pentane/ethyl ether, 3:1). Under GLC analysis conditions, however, VIII is completely transformed to IX, by a thermal rearrangement.[1]

By contrast, first-order kinetics is observed for the oxidation of anthracene (eq 1) under the same conditions, but at 40 °C (see Experimental Section).

Although the rate is very high in both cases, it is greater with VII than with anthracene: the different order of the reactions 1 and 3 can thus be attributable to the different rates at which the two substrates react with $^1O_2$. The reaction rate of VII with $^1O_2$ has been reported[5] to be larger than the $^1O_2$ decay rate.

RB^{2-} Immobilized on Silica Gel via an Anionic Exchange. Insoluble systems in which Rose Bengal is immobilized covalently have been reported: cross-linked polystyrene (Ⓟ-Rose Bengal, XI)[6] and silica gel (Ⓢ-Rose Bengal, XII).[7] These functionalized supports have been used in a variety of photooxidation reactions, including that of VII. There have also been reports[7] of the reuse of these systems through filtration of the insoluble matrix after the reaction.

We immobilized RB^{2-} on supports IIIa, IVa, and Va through an anionic exchange reaction conducted in water containing previously dissolved Na_2RB. As previously reported for the anion-exchange reactions of onium salts immobilized on silica gel,[13] systems IIIa–Va display a great affinity for soft anions and hence for the large, lipophilic RB^{2-}. The anionic exchange of system IIIa is illustrated in eq 5. As RB^{2-} climbs up the functionalized silica gel, it stains it purple, leaving the aqueous phase colorless. It is possible to obtain a load of RB^{2-} up to 10% of the degree of functionalization of the inorganic support.[14]



(5)

Like systems XI and XII, systems IIIb–Vb do not release RB^{2-} in solution nor into the environment of the reaction they have promoted. This shows that the ionic bond present is stable enough (as in the case of a covalent bond[7]), since both anion and cation are strongly lipophilic. Furthermore, in systems IIIb–Vb, RB^{2-} and the immobilized positive center can be separated and recovered through acidification.[15]

Like the commercially available XI, systems IIIb–Vb are effective heterogeneous photosensitizers. For example, reaction 4 was carried out, for comparison, under identical conditions (100 mg of 1,3-cyclohexadiene, 1.25 mmol, in 10.0 mL of dichloromethane, at 5 °C) using IIIb (320 mg, equivalent to 0.0125 mmol of sensitizer) or XI (42 mg, equivalent to 0.0125 mmol of Rose Bengal); after 15 min, 70% and 37% conversion, respectively, into the endoperoxide X was observed.

Table II offers a more extensive comparison between various catalysts of reaction 3, covering both soluble system (Ib and IIb, which are good PT catalysts and good micellar catalysts, respectively), and insoluble systems (IIIb, IVb, Vb, XI, and the Dowex-1 polystyrenic ion-exchange resin Ⓟ-$C_6H_4CH_2N^+(CH_3)_3Cl^-$).

The reactions of these catalysts were carried out in a variety of solvents, except for the polystyrenic resin XI and the Dowex-1, for which only chloroform was used.

For these polystyrene resin-based catalysts, activity is low in solvents with limited swelling properties.[9]

As in the case of the photooxidation of 1,3-cyclohexadiene, the data in Table II make it clear that in chloroform the very polar silica gel IIIb promotes photooxidation to a greater extent than the cross-linked organic polystyrene, whereas the Dowex-1 did not display any appreciable activity.

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(13) Tundo, P.; Venturello, P.; Angeletti, E. *J. Am. Chem. Soc.* **1982**, *104*, 6547–6551.

(14) For example, starting from IIIa with a functionalization degree of 0.44 mequiv of Br^-/g it is possible to obtain for IIIb a load of RB^{2-} up to 0.04 mmol/g. For system XII the highest load reported[7] was 0.007 mmol/g.

(15) Treatment of IIIb with 1 N HCl and washing it with methanol produced a colorless support. This support did not become purple after treatment with base and retained its anion-exchange properties.

Table II. Photooxidation of 5,6-Dihydro-2,3-diphenyl-*p*-dioxin (VII) (at 26 °C) in Various Solvents and Promoted by Rose Bengal Present in the Organic Phase by means of Different Carriers[a]

		% conversn in various solvents at specified times (in min)														
		cyclohexane			benzene			chloroform			acetonitrile			methanol		
entry	carrier	5	15	30	5	15	30	5	15	30	5	15	30	5	15	30
1	none									0[b]	56	100		46	96	
2	Ib[c]		11			89		79	100							
3	IIb[c]							28	99							
4	IIIb[d]	67	100		64	100		77[e]	100[e]		73	100		33	85	
5	IVb[d]		62	89		38	59		49	74		99	100		60	94
6	Vb[d]		13	22		14	35		31	69		45	86		37	72
7	XI[d]							16	43	76						
8	Dowex-1									1						

[a] VII, 50 mg; Rose Bengal, 0.01 molar equiv; solvent, 10.0 mL; H_2O, 2.0 mL (only for entries 2 and 3). For the analysis conditions, see Table I, footnote *b*. [b] After 2.0 h, 0% conversion. [c] 0.02 molar equiv. [d] The load of Rose Bengal on insoluble supports was (entry, mg/g of support): 4, 10; 5, 74; 6, 50; 7, 306; 8, 20. [e] With a higher load (40 mg/g instead of 10 mg/g), the conversion was 52% and 100% after 5 and 15 min, respectively.

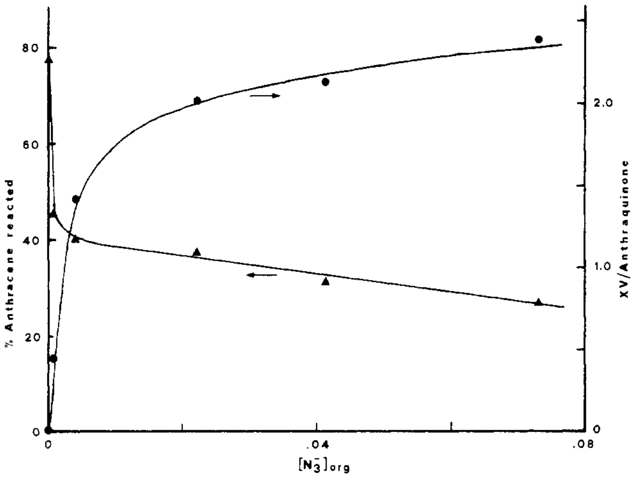


Figure 2. XV/anthraquinone ratio in reaction 8, carried out under PTC conditions and promoted by I, as a function of $[N_3^-]_{org}$ (right-hand scale, ●). Repressive effect of $[N_3^-]_{org}$ on conversion is shown in the left-hand scale (▲). Conditions: anthracene, 100 mg; H_2O, 2.0 mL; $CHCl_3$, 11 mL; $T = 40$ °C; Na_2RB, 0.01 molar equiv; Ia, 0.01, 0.03, 0.10, 0.50, 1.0, and 2.0 molar equiv, in that order, for the six experiments. When present, NaN_3 was 3.0 molar equiv. The ratios and the % conversions were determined by GLC after 3 h. $[N_3^-]_{org}$ was calculated from the value 0.24 of the Br^-/N_3^- partition constant (see Experimental Section).

The hydrophilic pyridinium salt IIb is less active than the corresponding lipophilic phosphonium salt Ib in the case of soluble systems. When, however, they are bound to silica gel, the pyridinium salt IIIb is more active than the corresponding phosphonium salt IVb. The latter, in turn, displays greater activity in the absence of a long spacer chain (IVb > Vb).

The results of Table II also indicate that the activity of the soluble system Ib, which is high in chloroform, falls markedly as the polarity of the solvent diminishes ($CHCl_3$ > C_6H_6 > C_6H_{12}), whereas the activity of the insoluble systems IIIb–Vb is much less sensitive to changes in the nature of the solvent. Moreover, the order of activity (IIIb > IVb > Vb) remains unchanged in the various solvents.

No loss of activity of IIIb was observed in reaction 3 conducted in chloroform at 0 °C, where it was repeatedly recycled after filtration. The results are given in Table III.

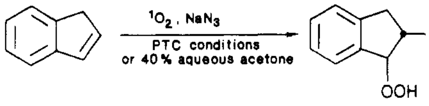
Reactions with Nucleophiles. When working in a double phase with a quaternary onium salt in the presence of RB^{2-}, even a nucleophile can be transferred into the organic phase. Following the PTC mechanism, it greatly increases its nucleophilic activity and hence can react with an intermediate, such as a dioxetane or endoperoxide.

Table III. Recycling IIIb in the Photooxidation of 5,6-Dihydro-2,3-diphenyl-*p*-dioxin (VII) (at 0 °C)[a]

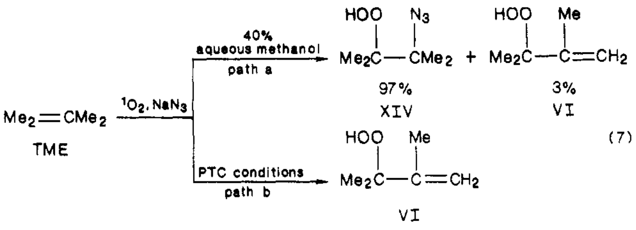
cycle	% conversn[b]	IIIb used (recovered), g
1	97	0.855[c]
3	86	(0.834)
5	96	(0.787)

[a] VII, 200 mg; $CHCl_3$, 10.0 mL. [b] After 20 min; for the analysis conditions, see Table I, footnote *b*; the reaction was always complete after 25 min. The product mixture contains only 5% of the diester IX. [c] Corresponding to 0.01 molar equiv of RB^{2-}

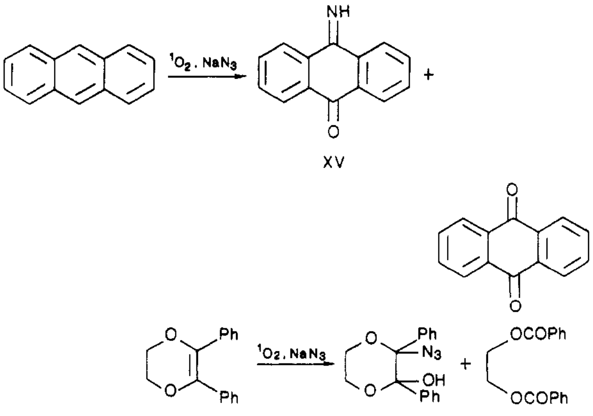
Accordingly, the reactions in eq 6–9 were performed in liquid–liquid (LL) PTC, with Ia as catalyst.



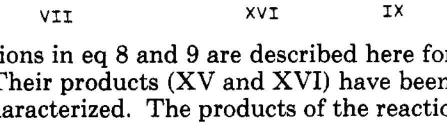
XIII (6)



(7)



(8)



VII XVI IX (9)

The reactions in eq 8 and 9 are described here for the first time. Their products (XV and XVI) have been isolated and characterized. The products of the reactions 6 and 7 were compared, by using TLC and GLC, with genuine samples obtained from the literature procedures.[11]

The reactions of $^1O_2$ with indene and TME in the presence of sodium azide have been investigated in mixed solvents (aqueous methanol and aqueous acetone) and

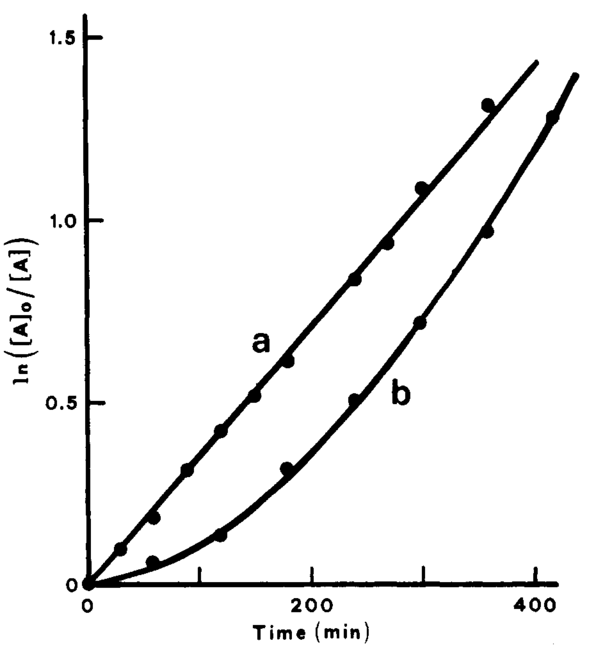


Figure 3. Photooxidation of anthracene at 40 °C with I in the presence of sodium azide (3.0 molar equiv) under PTC conditions: (a) Ia = 0.01 molar equiv, Ib = 0.04 molar equiv; (b) Ia = 0.48 molar equiv, Ib = 0.04 molar equiv. The other conditions were those reported in the Experimental Section for the photooxidation of anthracene according to eq 1.

have been reported[11] to give rise to organic azides as shown in eq 6 and 7 (path a). In such conditions has been reported that the reaction of TME involves radical intermediates.[16]

Under PTC conditions, TME, on the other hand, shows no trace of XIV but gives only allyl hydroperoxide VI (eq 7 path b).

Indene forms product XIII under PTC conditions three times faster than in aqueous acetone (see Experimental Section).

As previously stated, the reaction between $^1O_2$ and anthracene gives anthraquinone (eq 1). If N_3^- is present and under anionic activation conditions (eq 8), one also obtains the imino derivative XV, probably through elimination of N_2 and migration of hydrogen (Curtius rearrangement); in the Experimental Section, a preparative-scale reaction is described.

Product XV decomposes rapidly on silica or alumina but is stable under the reaction[17] or GLC conditions; quantitative measurements can thus be carried out on the reaction mixtures. The ratio between XV and anthraquinone produced, according to eq 8, increases as $[N_3^-]_{org}$ increases, though not in a linear manner: as shown in Figure 2 on the right-hand scale, the ratio reaches 2.4 when $[N_3^-]_{org}$ is 7.3×10^{-2}. Figure 2 also shows (on the left-hand scale) the repression of the anthracene conversion attributable to the quencher characteristics of the N_3^- ion on $^1O_2$.[18]

The anthracene photooxidation kinetics was also investigated in anionic activation, under the same conditions used for the photooxidation without nucleophiles (see Experimental Section), by using two different $[N_3^-]_{org}$. Figure 3a corresponds to the second point of Figure 2 ($[N_3^-]_{org} = 5.1 \times 10^{-4}$), while Figure 3b is equivalent to the fourth point ($[N_3^-{}_{org} = 2.2 \times 10^{-2}$). As can be seen in Figure 3a, the reaction rate follows a first-order kinetics as without nucleophile. In Figure 3b, on the other hand, the kinetics is no longer first-order and the better reaction order is 0.4 ($r = 0.9999$).

As shown in Table III, the dioxetane intermediate VIII can easily be isolated in the reaction solvent by working with an insoluble catalyst. The dioxetane VIII isolated in $CHCl_3$ under these conditions gave benzil by using PhS^- or SCN^- as nucleophiles and Ia as PT catalyst. Other not yet identified compounds were obtained with Ph_3P, CN^-, and OH^-. This screening showed a wide variety of reactivity behaviors; some of them could not be observed in the conditions where VIII was formed. One meaningful example is the reaction of VIII with N_3^-. Under two-phase conditions and in a single step (eq 9, see Experimental Section), the cyclic azido derivative XVI was obtained together with the diester IX. On the other hand, this azido derivative was not obtained when starting from VII in the presence of a 2,6-di-*tert*-butylphenol derivative (tetrakis[((3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyl)oxy)methyl]methane, Irganox 1010) as radical inhibitor (one-step procedure) nor from the reaction of dioxetane VIII with N_3^- under anionic activation conditions (two-step procedure); in both cases, a common, as yet unidentified, new azido derivative was obtained (see Experimental Section).

Both the one-step and two-step procedures and radical inhibition are selective.

Discussion

Some advantages are obtained when an anionic sensitizer is used in the organic phase of LL-PTC as the counteranion of a lipophilic onium salt.

In the first place, the reaction mixture is easier to prepare: from the operational standpoint, it is sufficient to add to a two-phase (water and organic solvent) system a quantity of onium salt effectively stoichiometric with respect to the sensitizer to obtain the quantitative transfer of RB^{2-} into the organic phase.[19] These catalysts and these conditions have proved capable of promoting the formation of $^1O_2$ when working in the presence of $^3O_2$ and light and hence the photooxidation of organic substrates (eq 1–4). Moreover, in all the reactions carried out under LL-PTC the bleaching of the sensitizer was never observed. In addition, the rate observed under LL-PTC conditions (Table I) was higher than that observed in the same apparatus using previously reported methods (mixed solvents,[11,12] complexing systems,[4] and liposoluble Rose Bengal derivatives[5]). This increase in activity can probably be ascribed to several factors, including the use of less polar solvents and the presence of RB^{2-} as separate ion pairs rather than aggregates.

From previous PTC studies we know[8] that the use of lipophilic onium salts activates the anion they carry into the organic phase, by increasing its free energy. In addition, the presence of bulky alkyl chains that quaternarize the heteroatom (by comparison with the cations of alkaline metals) greatly reduces the formation of molecular aggregates.[20]

In many respects, a similar phenomenon is described here for the anionic photosensitizers, such as Na_2RB, which are water-soluble salts. $^1O_2$ photooxidation of organic

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[16] (a) Foote, C. S.; Fujimoto, T. T.; Chang, Y. C. *Tetrahedron Lett.* **1972**, *1*, 45–48. (b) Hasty, N.; Merkel, P. B.; Radlick, P.; Kearns, D. R. *Tetrahedron Lett.* **1972**, *1*, 49–52.

[17] Conversion of XV into anthraquinone is less than 10% after 2 h.

[18] Lindig, B. A.; Rodgers, M. A. J. *Photochem. Photobiol.* **1981**, *33*, 627.

[19] If Ia is less than 2.0 molar equiv with respect to RB^{2-} the aqueous solution remains colored.

[20] Landini, D.; Maia, A.; Montanari, F. *Nouv. J. Chim.* **1979**, *3*, 575.

substrates promoted by these sensitizers, in fact, has usually been carried out in mixed aqueous–organic solvents capable of solubilizing the organic substrate as well. The use of protic solvents, however, retards some of these reactions. Under LL-PTC conditions one can also work with poorly polar solvents, where it has been reported[21] that $^1O_2$ has a longer lifetime (solvent, $t_{1/2}$ in μs: methanol, 7; cyclohexane, 17; benzene, 24; acetonitrile, 30; chloroform, 60).

Increasing the lipophilicity of Rose Bengal (e.g., Rose Bengal bis(triethylammonium) salt, Rose Bengal benzyl ester triethylammonium salt, Rose Bengal ethyl ester triethylammonium salt, and Rose Bengal octyl ester tri-*n*-butylammonium salt) increases its solubility in low polar solvents, but, as Neckers has reported,[5] these derivatives form aggregates too.

The ratio ϵ_1/ϵ_2 reported in Figure 1 is an indication of excimer formation and so of the presence of aggregates: in fact, it decreases when the dye concentration is increased. When Rose Bengal octyl ester tri-*n*-butylammonium salt is used, a value of 0.86 for ϵ_1/ϵ_2 has been observed in toluene and 3.13 in methanol.[5] By contrast, in apolar organic solvents, too, if RB^{2-} is the counteranion of bulky quaternary onium salts, ϵ_1/ϵ_2 is always high (Figure 1: chloroform, 3.60; toluene, 2.81; cyclohexane (not shown), 3.33). One can conclude that under LL-PTC conditions aggregates are avoided, excimers do not form, and the energy transfer can thus take place more effectively.

The advantages of using immobilized RB^{2-} on silica gel functionalized onium salts are as follows: (i) rapid preparation of a support with the established RB^{2-} load; (ii) removal of RB^{2-} from the insoluble support.

Furthermore, these systems benefit from the advantages peculiar to insoluble catalysts insofar as they can be removed from the mixture by filtration when the reaction is over. In addition, silica gel, when used as the insoluble support, does not undergo appreciable swelling (unlike polystyrenic resins) and hence can be used in all solvents. In keeping with this, systems IIIb, IVb, and Vb proved able to promote reactions 3 (Table II) and 4 with an activity that was comparable and at times superior to that of soluble onium salts. Moreover, it has been shown that the catalytic activity of insoluble system IIIb remains constant when it is recycled several times (Table III).

Three points should be borne in mind when considering the influence of the insoluble support on photosensitizer activity: (i) a different RB^{2-} load on the support has a greater influence on catalytic activity than in solution, since excimers are more easily formed on account of the higher local concentration (compare footnote *e*, Table II); (ii) both the support and a high load of immobilized onium salt may screen RB^{2-} from the light; (iii) nevertheless, insoluble systems can determine the environment in which the reactions they promote take place. In our case, this environment is the microenvironment of the functionalized silica support, because it is here that the RB^{2-} is present.[22]

These considerations offer an interpretation of the data in Table II. The poor reactivity of RB^{2-} immobilized on an ion-exchange resin (Dowex-1, entry 8), in fact, may be due to its high affinity for water, which generates a microenvironment little appropriate to the reaction ($^1O_2$ lifetime in water is 2 μs[21]). In addition, the organic substrate may be excluded from this strongly aqueous environment. The high activity recorded in Table II for insoluble systems IIIb–Vb is attributable, as in the case of the corresponding soluble salts, to the fact that there are no RB^{2-} aggregates.

The differences between IIIb, IVb, and Vb are difficult to explain. The greater activity of IIIb compared with IVb cannot be simply put down to the presence of a pyridinium salt, because the opposite is true of the corresponding soluble salts (cf. entries 2 and 3); an effect of the insoluble matrix must therefore be invoked.

There is a striking difference between RB^{2-} immobilized on silica and that transported by I with regard to the change in activity noted on passing from polar to apolar solvents. Whereas reaction 3 is already complete after 15 min with system IIIb whether in chloroform, benzene, or cyclohexane (entry 4), with system Ib there is only 11% conversion after the same time in cyclohexane, as opposed to 89% in benzene and 100% in chloroform (entry 2).

This effect is probably due to the greater constancy of the microenvironment in which the reaction takes place, since the insoluble support contributes with the solvent to determine its nature.

For the moment, it is not yet clear what this microenvironment is in systems IIIb–Vb nor how it influences the excitation of RB^{2-}, the transfer of energy to $^3O_2$, and the lifetime of $^1O_2$. This topic is under investigation.

Reactions with Nucleophiles. Since RB^{2-} is transferred by an effective PT catalyst, reactions with nucleophiles can also be carried out at the same time and under the same conditions.

Although the objectives are different, in this case there is activation of both the RB^{2-} and the nucleophilic anion.

A photooxidation product having a dioxetanic or endoperoxidic structure and a sufficiently long lifetime is able to react with a nucleophile due to the effect of the ring strain; moreover, the classic S_N2 is more easily obtained if the anion is activated.

The reaction products of a nucleophilic displacement can also provide some information about the mechanism: the structure and mechanism of formation of the first product of the reaction of $^1O_2$ with alkenes and dienes is still the subject of close study,[23] including its theoretical aspects.[24]

LL-PTC conditions provide a clear discrimination, as shown for reactions 6 and 7 (path a), between a reaction pathway involving a photooxidation intermediate (initial attack of $^1O_2$ on a π system) and a radical one (initial attack of $N_3^{\bullet}$ radical). If a $CHCl_3/N_3^-{}_{aq}$ two-phase system is used, TME only gives the normal hydroperoxide (VI), whereas indene gives the azido derivative XIII. Hydroperoxide is observed with or without azide in the presence of radical inhibitors (see Experimental Section).

Nucleophilic substitution products can be obtained in LL-PTC if dioxetanic (as in the case of indene) or endoperoxidic intermediates are present. The second situation arises in the reaction of anthracene with $N_3^-{}_{aq}$; it yields the imino derivative XV, as well as anthraquinone (eq 8).[25]

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[21] Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244–7253.

[22] Other factors [not possible for the rigid silica backbone which is only externally functionalized (see ref 10c)] are present for polystyrene-immobilized Rose Bengal where the swelling of the resin is important on the quenching of internal (see ref 9b) sensitizer molecules. As Neckers has reported (see: Paczkowska, B.; Paczkowski, J.; Neckers, D. C. *Macromolecules* **1986**, *19*, 863–870), in such functionalized resins oxygen diffusion is rate-determining.

[23] Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359–387.

[24] (a) Tonachini, G.; Schlegel, H. B.; Bernardi, F.; Robb, M. A. *Theochem.* **1986**, *138*, 221–227. (b) Hotokka, M.; Roos, B.; Siegbahn, P. *J. Am. Chem. Soc.* **1983**, *105*, 5263 and references therein.

[25] The fact that reaction 8 is not inhibited by radical quenchers shows its ionic character: both in methanol and under the conditions of Figure 3b, addition of 0.25 molar equiv of Irganox 1010 had no effect on the composition of the products.

If azide is present, the reaction rate is lower (Figure 2, left), because (as already mentioned)[18] the N_3^- ion acts as $^1O_2$ quencher.

The ratio XV/anthraquinone, as expected, increases as the $[N_3^-]_{org}$ increases, until a plateau is reached (Figure 2, right); this behavior can be kinetically explained with the reaction of bases (RB^{2-} and N_3^-) with the endoperoxide intermediate (supplementary material).

The presence of a common endoperoxide intermediate in the reactions carried out with or without N_3^- is also indicated by the kinetics. In the absence of N_3^-, anthracene has a first-order kinetics ($k = 6.1 \times 10^{-2}$ min^{-1} for $[RB^{2-}] = 1.12 \times 10^{-3}$); the first-order kinetics is maintained (Figure 3a), albeit with a lower rate ($k = 3.6 \times 10^{-3}$ min^{-1} for $[RB^{2-}] = 1.12 \times 10^{-3}$), when $[N_3^-]_{org}$ is low. In the presence of azide ions, too, the reaction of $^1O_2$ with anthracene produces the same intermediate which, in turn, reacts with the activated nucleophile.

Higher $[N_3^-]_{org}$ values lead to a lower reaction order. This can be due to radical incursions occurring at high $[N_3^-]_{org}$ and shows the complex character of this reaction.

Photooxidation of VII in the presence of N_3^- yields different products when carried out in one or two steps under the same PTC conditions (see Experimental Section). This unexpected result indicates that radical intermediates may also be present, in contrast with the reaction of TME, also under PTC conditions.

Taken as a whole, these results show that PTC can throw light on some aspects of the photooxidation reaction. At the same time, however, it reveals certain complexities: e.g., the different behavior of TME and VII. Comparison between the results obtained with TME and indene shows that PTC clarifies the mechanism of their reactions.

Conclusions

Both practical and speculative consequences derive from the use of classic PT catalysts to render Rose Bengal soluble in poorly polar solvents. From the practical standpoint, the reaction mixture is easier to prepare, high reaction rates are observed (due to RB^{2-} as ion pair and a longer $^1O_2$ lifetime), and it is possible to operate simultaneously in the presence of nucleophiles. This may be of assistance in the organic synthesis of compounds hard to obtain in other ways. On the speculative side, PTC aids the study of the mechanism followed by these complex reactions.

The ready immobilization of RB^{2-} on functionalized silica gel by means of an anionic exchange reaction has shown that these objectives can also be reached with an immobilized catalyst.

New opportunities could be opened if PTC conditions are used in photooxidation reactions promoted by sensitizers. Further investigation of the reaction mechanism and the application of our results in organic synthesis is now in progress.

Experimental Section

General Methods. Nuclear magnetic resonance spectra were recorded on a Hitachi Perkin-Elmer R-24B 60-MHz ^1H NMR spectrometer. Gas chromatographic analyses were conducted on a Varian Vista 6000 gas chromatograph equipped with a Varian CDS 111 integrator. Infrared spectra were obtained with a Perkin-Elmer 1710 FTIR spectrometer. Electronic absorption spectra were measured with a Varian DMS 100 UV–vis spectrophotometer, and mass spectra were obtained with a Kratos-AEI MS 80 spectrometer.

All organic and inorganic reagents were ACS grade and used without purification. 5,6-Dihydro-2,3-diphenyl-*p*-dioxin was obtained according to the literature.[26]

Rose Bengal bound covalently on polystyrene (XI) was commercial (Fluka).

Photooxidation Apparatus and Procedure. A 25-mL, double-jacket, three-neck, Pyrex reaction flask was charged with the solvent, the substrate to be oxidized, and the photosensitizer; the reaction mixture was magnetically stirred and thermostated by continuous circulation of a water–ethylene glycol mixture (Neslab RTE-5B thermostat). Oxygen was bubbled in the solution (at atmospheric pressure) at a rate of 20 mL/min. The flask was irradiated with a 500-W tungsten halogen lamp, placed at 19 cm (filament center of the flask).

Immobilization via Anion Exchange of RB^{2-} on Silica Gel Functionalized with Onium Salts IIIb, IVb, and Vb. The starting functionalized supports IIIa, IVa, and Va had a titer of 0.44, 0.72, and 0.49 mequiv of Br^-/g, respectively. A given quantity of Na_2RB (up to 0.1 molar equiv with respect to the immobilized onium salt) was dissolved in 50 mL of water. Then the functionalized support (up to 10 g) was added, and the suspension was slowly stirred in a Erlenmeyer flask until the aqueous solution became colorless (the time required, 1–5 h, depends on the RB^{2-}/onium salt ratio). The silica gel was then filtered and washed with water and methanol. The solid was extracted in a Soxhlet with hot methanol until it remained colorless. Depending on the Na_2RB used, IIIb, IVb, and Vb had a load of 0.010, 0.072, and 0.049 mmol RB^{2-}/g. The Dowex-1 resin (Dow Chem. Co., 3.5 mequiv of Cl^-/g, dry) was functionalized in the same way (Table II, entry 8).

Photooxidation of 5,6-Dihydro-2,3-diphenyl-*p*-dioxin (VII, eq 3). The reaction flask was charged with 10.0 mL of chloroform, 50 mg (0.21 mmol) of VII, 0.85 mg (1.7×10^{-3} mmol, 8×10^{-3} molar equiv) of Ia and 30 mg of eicosane as internal standard; 2.0 mL of water containing 0.86 mg (0.84×10^{-3} mmol, 4×10^{-3} molar equiv) of Na_2RB were added.

The mixture was then photooxidized at 26 °C.

Every 2 min, 0.10-mL samples were withdrawn and diluted with 1.0 mL of ethyl ether; addition to this solution of 0.15 g of silica gel removed the onium salt.

The concentration of VII was determined by GLC in comparison with the internal standard. The last sample (taken at 10 min) showed that the reaction was already complete.

A zero-order rate constant was obtained ($k = 2.1 \times 10^{-3}$ M min^{-1}; $r = 0.999$).

Photooxidation of Anthracene (eq 1). The reaction flask was charged with 10.0 mL of chloroform, 100 mg (0.562 mmol) of anthracene, 11.4 mg (0.0225 mmol, 0.04 molar equiv) of Ia, and 50 mg of eicosane as internal standard. Then 2.0 mL of water containing 11.4 mg (0.0112 mmol, 0.02 molar equiv) of Na_2RB was added. The mixture was photooxidized at 40 °C. Samples (0.10 mL) were withdrawn at suitable time intervals and analyzed as previously described for VII; the anthracene concentration was determined in comparison with eicosane. A first-order rate constant was obtained ($k = 6.2 \times 10^{-2}$ min^{-1}; $r = 0.999$).

Photooxidation of Indene in PTC and Aqueous Acetone Conditions in the Presence of Sodium Azide. The reaction flask was charged with 6.0 mL of chloroform, 100 mg (0.86 mmol) of indene, 0.44 g (0.86 mmol, 1.0 molar equiv) of Ia, and 50 mg of *n*-dodecane as internal standard. Then 2.0 mL of water containing 8.7 mg (8.6×10^{-3} mmol, 0.01 molar equiv) of Na_2RB and 112 mg (1.72 mmol, 2.0 molar equiv) of NaN_3 was added. The mixture was photooxidized at 40 °C. After 5.5 h, the GLC analysis showed a conversion of 77% to the azido derivative XIII.

XIII was also obtained by operating in aqueous acetone, according to the literature (9.0 mL of acetone, 6.0 mL of water, 100 mg of indene, 8.7 mg of Na_2RB, and 112 mg of NaN_3), but the reaction rate was much lower: 83% of conversion after 17 h.

Photooxidation of 2,3-Dimethyl-2-butene (TME) in PTC and Aqueous Methanol Conditions in the Absence and in the Presence of Sodium Azide. The reaction flask was charged with 10.0 mL of chloroform, 100 mg (1.20 mmol) of TME, and 12.2 mg (0.024 mmol, 0.02 molar equiv) of Ia. Then 2.0 mL of water containing 12.2 mg (0.012 mmol, 0.01 molar equiv) of Na_2RB was added. The mixture was photooxidized at 5 °C. After 30

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[26] Summerbel, R. K.; Berger, D. R. *J. Am. Chem. Soc.* **1959**, *81*, 633.

min, the GLC analysis showed a residual TME less than 2% and the appearance of a single compound corresponding to the allyl hydroperoxide VI.

When the reaction is carried out in the presence of 0.156 g (2.40 mmol, 2.0 molar equiv) of NaN_3, the rate was lower: after 3 h the conversion was about 50%. No trace of azido hydroperoxide XIV was observed (as observed when the reaction is carried out in 40% aqueous methanol) the only product was the allyl hydroperoxide obtained without azide. Similar results (no azido derivative) were obtained when working in aqueous methanol but in the presence of 0.25 molar equiv of a radical inhibitor (Irganox 1010).

Photooxidation of Anthracene in the Presence of Sodium Azide under PTC Conditions (eq 8). Synthesis of 10-Imino-9(10*H*)-anthracenone. A reaction flask (250 mL instead of 25 mL, for preparative purposes) was charged with 60 mL of chloroform, 2.0 g (11.2 mmol) of anthracene, 11.4 g (22.4 mmol, 2.0 molar equiv) of Ia, 10 mL of water, 3.64 g (56.0 mmol, 5.0 molar equiv) of NaN_3, and 0.114 g (0.112 mmol, 0.01 molar equiv) of Na_2RB. The reaction mixture was photooxidized at 40 °C. After 24 h, the reaction was complete. The aqueous phase was separated, and the organic phase was washed twice with water.

After drying, the solvent was removed under vacuum and the mixture chromatographed on silica gel, by eluting with chloroform–ethanol (95:5). Since 10-imino-9(10*H*)-anthracenone (XV) decomposes into anthraquinone on silica gel and moreover its R_f is lower than anthraquinone, the fractions of XV collected were impure (10% of anthraquinone). Obtained was 1.44 g of yellow needles (yield, 55%). Analytical samples of XV (anthraquinone 3%) were obtained by further crystallizations from methanol, where anthraquinone is less soluble: mp 110 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.5–8.5 (double m); mass spectrum, *m/e* 207 (M^+); IR ($CHCl_3$) 1668 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_9NO$ (H): 4.38. Found: 4.28. Calcd (N): 6.76. Found: 6.54. (Calcd with 3% of anthraquinone: N, 6.56.)

Photooxidation of 5,6-Dihydro-2,3-diphenyl-*p*-dioxin (VIII) in the Presence of Sodium Azide and under PTC Conditions (eq 9). Synthesis of 3-Azido-5,6-dihydro-2,3-diphenyl-1,4-dioxin-2-ol (XVI). The 250-mL reaction flask was charged with 100 mL of chloroform, 4.0 g (16.8 mmol) of VII, 8.5 g (16.8 mmol, 1.0 molar equiv) of Ia, 10 mL of water, 5.46 g (84 mmol, 5.0 molar equiv) of NaN_3, and 0.170 g (0.168 mmol, 0.01 molar equiv) of Na_2RB. The reaction was complete after photooxidation at 40 °C for 24 h; the diester IX was the main product (TLC). The aqueous phase was separated, and the organic phase was washed twice with water. After drying, the solvent was removed under vacuum and the mixture chromatographed on silica gel, by eluting with petroleum ether–ethyl ether (from 90:10 to 10:90). Obtained was 1.4 g of XVI (yield, 28%). XVI crystallizes from ethanol: mp 125–127 °C; ^{1}H NMR ($CDCl_3$) δ 7.15 (br s, 10 H), 4.7–3.5 (m, 4 H), 2.8 (s, hydroxyl, 1 H); IR (Nujol) 3380 (OH), 2115 (N_3) cm^{-1}; mass spectrum, *m/e* 269 (M – N_2), 255 (M – N_3). Anal. ($C_{16}H_{15}N_3O_3$) C, H, N.

The reaction carried out on a smaller quantity of VII (50 mg) and under the same conditions used for the synthesis of XVI but in the presence of Irganox 1010 (0.5 molar equiv with respect to VII) as radical inhibitor did not yield XVI; the only azido derivative was that corresponding to the compound obtained in two steps (see below).

Reaction of VII with N_3^- through the Intermediate VIII Carried Out in Two Steps. After photooxidation of 0.4 g (1.68 mmol) of VII, carried out according to the conditions of Table III, the chloroform solution of VIII (10 mL, containing about 5% of IX) was reacted in PTC conditions in the dark: 2.0 mL of water containing 2.9 molar equiv of NaN_3 was added, and the two phases were stirred for 4 h at 0 °C and in the presence of 0.5 molar equiv of Ia.

The reaction mixture was chromatographed on silica gel, eluting with petroleum ether–ethyl ether (from 9:1 to 3:2). The main product was the diester IX; the only azido derivative had a R_f close to that of XVI. Obtained was 104 mg of an oil: ^{1}H NMR ($CDCl_3$) δ 7.1–8.2 (m, 13 H), 4.6 (s, 4 H); IR (neat) 3420 (OH), 2120 (N_3), 1720 (C=O) cm^{-1}; mass spectrum, *m/e* 270, 256 (compare mass spectrum of XVI, *m/e* 269 and 255, respectively).

This compound, as XVI, gives benzil by hydrolysis in strong acidic media.

Partition of Br^-/N_3^- in the Chloroform–Water Two-Phase System. NaN_3 (25.0 mL, 0.060 M) in water was added to 25.0 mL of a 0.060 M solution of Ia in chloroform. After the mixture was shaken for 5 min and allowed to stand for 30 min, 10 mL of the aqueous phase was potentiometrically titrated (0.1 N $AgNO_3$).

The equilibrium constant (K) for the reaction

$$N_3^-{}_{aq} + Br^-{}_{org} \rightleftarrows N_3^-{}_{org} + Br^-{}_{aq}$$

was determined from the calculated $[N_3^-]_{aq}$ and $[Br^-]_{aq}$:

$$K = \frac{[N_3^-]_{org}[Br^-]_{aq}}{[N_3^-]_{aq}[Br^-]_{org}} = 0.24$$

An identical value was obtained for concentrations of Ia and NaN_3 corresponding to the fifth point of Figure 3 (10 mL of 0.112 M solution of Ia in chloroform and 3.0 mL of 0.56 M solution of NaN_3 in water).

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Registry No. Ia, 14937-45-2; IIa, 140-72-7; VI, 13249-73-5; VII, 4344-45-0; IX, 94-49-5; XIII, 108295-22-3; XV, 4392-73-8; XVI, 108295-21-2; Na_2RB, 632-69-9; anthracene, 120-12-7; 2,3-dimethyl-2-butene, 563-79-1; indene, 95-13-6; 1,3-cyclohexadiene, 592-57-4.

Supplementary Material Available: Kinetics analyses and derivations concerning the data in Figure 3 (3 pages). Ordering information is given on any current masthead page.