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Reductive PET Cycloreversion of Oxetanes: Singlet Multiplicity, Regioselectivity, and Detection of Olefin Radical Anion

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Received June 24, 2003

Cycloreversion of 2-(*p*-cyanophenyl)-4-methyl-3-phenyloxetane (**1**) is achieved using 1-methoxynaphthalene (**2**) as electron-transfer photosensitizer. The experimental results are consistent with the reaction taking place from the singlet excited state of the sensitizer. Ring splitting of the radical anion $\mathbf{1}^{\bullet-}$ occurs with cleavage of O−C$_2$ and C$_3$−C$_4$ bonds, leading to products (acetaldehyde and *p*-cyanostilbene) different from the reagents used in the Paterno−Büchi synthesis of **1**. The olefin radical anion involved in the electron-transfer process has been detected by means of laser flash photolysis.

Introduction

During the past few decades, photoinduced electron transfer (PET) processes have attracted considerable interest.[1] They have been intensively studied as fundamental steps in mechanistic and synthetic organic photochemistry and appear to be involved in key biological processes.

Cycloreversion (CR) of oxetanes by PET is important for the photoenzymatic repair of the (6−4) photoproducts of the DNA dipyrimidine sites by photolyase.[2−5] The oxidative version of this reaction has been achieved using cyanoaromatics, chloranil or (thia)pyrylium salts as electron-transfer photosensitizers.[6−11] In the case of the (thia)pyrylium salts, CR takes place from the triplet excited state of the photosensitizer and may lead to products different from the reagents employed in the Paterno−Büchi photocycloaddition to synthesize the oxetanes. In addition, radical cation intermediates have been detected by laser flash photolysis (LFP).

Only a few reports have appeared on the CR of oxetane radical anions despite their higher biological interest.[2] Kim et al.[12−14] have pointed out that the repair of the (6−4) photoproducts of DNA follows a mechanism analogous to the reductive electron-transfer established for cyclobutane pyrimidine DNA dimers. Falvey et al.[2,15−17] have proposed that reversal of the (6−4) photoproduct to the oxetane intermediate is followed by the photochemical step involving transfer of one electron from a FADH$^-$ cofactor to the resulting oxetane. The oxetane radical anion then cleaves to provide two pyrimidine units (one of them as radical anion).

To evaluate the proposed mechanism, cycloadducts of 1,3-dimethylthymine with benzaldehyde and benzophenone have been used as model systems and reacted with a variety of electron-donor photosensitizers. This has led to LFP detection of the radical anion of the carbonyl fragment, a clear proof in support of a PET mechanism. On the basis of the fact that fluorescence of the photosensitizer is quenched by the oxetanes, it has been proposed that the reaction takes place from the singlet excited state of the former.

In connection with the mechanistic aspects of the reductive PET CR of oxetanes, the following questions remain still open and deserve further investigations: (i) the multiplicity of the involved excited state, as the

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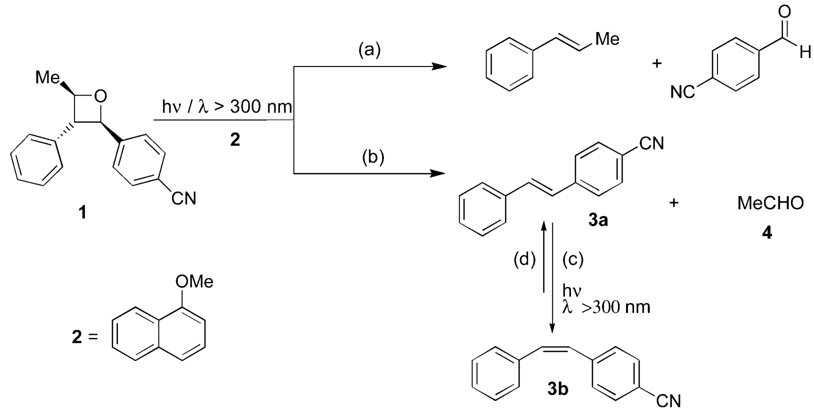
10.1021/jo034890n CCC: $25.00 © 2003 American Chemical Society
Published on Web 12/03/2003

SCHEME 1



occurrence of fluorescence quenching may or may not be associated with the actual ring splitting reaction, (ii) the location of spin and charge in the intermediates, as in principle the radical anion of the olefin fragment could also be formed, and (iii) the regioselectivity of CR, with special attention to the possibility of cleavage leading to products different from the reagents used for the Paterno–Büchi synthesis of oxetanes.

Therefore, in the present work, the behavior of 2-(*p*-cyanophenyl)-4-methyl-3-phenyloxetane (**1**) under electron-transfer conditions has been examined. By contrast with previous results on 2-phenyl and 2,2-diphenyl systems,[15–17] the 2,3-diphenyl substitution could result in the formation of stilbenes, as it has been observed for the oxidative CR of oxetanes.[7–9] On the other hand, the electron-withdrawing substituent at the 2-phenyl group could stabilize the olefin radical anion relative to the carbonyl-derived species. 1-Methoxynaphthalene (**2**) has been chosen as photosensitizer in view of its good electron-donor properties[18] ($E^*_{D^{\bullet+}/D} = -2.49$ V).

The PET process between **1** and **2** has been studied in detail in order to gain further insight into the mechanistic aspects of the reductive CR of oxetanes. Although both singlet and triplet quenching have been observed, the calculated free energy changes, together with product studies in the presence of triplet quenchers, clearly support involvement of the singlet excited state in the electron-transfer reaction. These studies have provided clear evidence for the involvement of olefin radical anion intermediates.

Finally, instead of leading to the retro-Paterno–Büchi process (Scheme 1, pathway a), the reaction proceeds with the opposite regioselectivity with cleavage of the O–C$_2$ and C$_3$–C$_4$ bonds (Scheme 1, pathway b).

Results and Discussion

Steady-State Irradiations. Oxetane **1** was prepared by Paterno–Büchi photocycloaddition of β-methylstyrene to *p*-cyanobenzaldehyde.[11] It was irradiated ($\lambda = 300$ nm) in acetonitrile, under argon, in the presence of catalytic amounts of 1-methoxynaphthalene (**2**). The reaction was followed by ^{1}H NMR and GC–MS and resulted in the production of *cis*-*p*-cyanostilbene (**3b**) as main photoproduct, together with small amounts of *trans*-*p*-cyanostilbene (**3a**). The **3b**/**3a** ratio after 30 min of irradiation was found to be ca. 4/1. Acetaldehyde (**4**) was also detected. To check whether **3b** could be formed from **3a** by a rapid trans–cis isomeration, solutions of both isomers were separately irradiated in the presence of **2** under the same conditions. In the two cases, photoequilibrium mixtures strongly shifted toward **3b** were obtained. Thus, the reductive PET reaction of oxetane **1** follows pathways b + c of Scheme 1. These results contrast with previous reports,[2,15–17] where CR of oxetane radical anions with different substitution exhibits the opposite regioselectivity, leading to the Paterno–Büchi precursors (Scheme 1, pathway a).

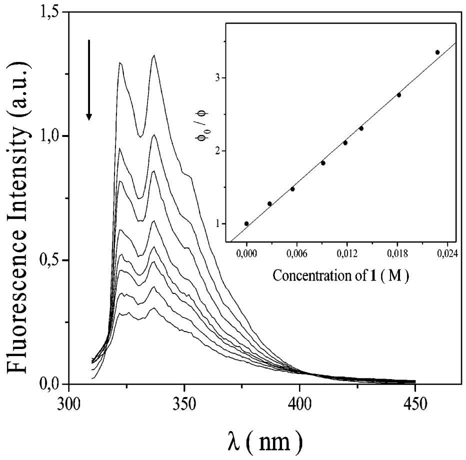


FIGURE 1. Quenching of the fluorescence of **2** in the presence of increasing amounts of **1**. Inset: Stern–Volmer plot to obtain $k_q(S_1)$.

Fluorescence Quenching. To disclose the nature of the excited state involved in the PET process, the fluorescence of 1-methoxynaphthalene (**2**) was studied in the presence of increasing amounts of **1**.

The fluorescence intensity gradually decreased (see Figure 1), indicating significant quenching by the oxetane. The quenching rate constant $k_q(S_1)$ was obtained from the Stern–Volmer analysis (eqs 1 and 2, inset of Figure 1):

$$\Phi_0/\Phi = 1 + K_{SV}[\text{oxetane}] \tag{1}$$

$$K_{SV} = \tau_s k_q(S_1) \tag{2}$$

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The value of the Stern−Volmer constant (K_{SV}) was found to be 101 M^{-1}. Taking into account the fluorescence lifetime (τ_s) reported for **2** in acetonitrile (13.6 ns), [18a] the rate constant for singlet quenching can be estimated as $k_q(S_1) = 7.4 \times 10^9$ M^{-1} s^{-1}. From these data, oxetane **1** quenches the fluorescence of **2** at a nearly diffusion controlled rate.

Based on the $k_q(S_1)$ value, the relative contributions of the competing pathways resulting in the deactivation of the singlet excited state of **2** in the presence of different concentrations of **1** were determined: fluorescence emission, fluorescence quenching, and intersystem crossing. Competition between them should be governed by the respective rate constants and by the quencher concentration.

The rate constant of fluorescence (k_f) and intersystem crossing (k_{isc}) are intrinsic properties of the photosensitizer. The values for **2** were calculated from eqs 3 and 4, where the quantum yields of fluorescence (Φ_f) and intersystem crossing (Φ_{isc}) have been taken as 0.36 and 0.64, respectively.[19] The resulting values for the rate constants were $k_f = 2.6 \times 10^7$ s^{-1} and $k_{isc} = 4.7 \times 10^7$ s^{-1}, respectively.

$$\tau_s k_f = \Phi_f \tag{3}$$

$$\tau_s k_{isc} = \Phi_{isc} \tag{4}$$

Hence, under the preparative irradiation conditions ([**1**] = 10^{-2} M), quenching of the excited singlet of **2** by **1** is the major deactivation pathway (50%). However, under these conditions there is still some residual fluorescence (18%), and a significant amount of excited molecules (32%) intersystem cross to the excited triplet state. Therefore, the observation of fluorescence quenching alone does not allow to rule out the possibility that the PET CR of oxetane **1** could take place from the excited triplet state of the photosensitizer.

Time-Resolved Studies. The possible involvement of the sensitizer triplet state in the electron-transfer reaction depends on both the triplet yield and the rate constant of triplet quenching. As the triplet of **2** is significantly populated even in the presence of **1**, it could in principle be reactive excited state. The feasibility of this hypothesis was checked by means of LFP. Excitation of **2** at 308 nm resulted in an intense peak at 435 nm, which was assigned to the characteristic triplet−triplet absorption of **2**.[19] This experiment was also performed upon addition of increasing amounts of **1** to identify the possible transient reaction intermediates and to determine the triplet quenching rate constant. In the presence of **1**, a diminished absorption at 435 nm was observed and a new intense signal appeared around 500 nm which was tentatively assigned to the *trans*-*p*-cyanostilbene radical anion (**3a**$^{\bullet-}$) (Figure 2).

To confirm the assignment, this species was independently generated from its neutral precursor. For this purpose, 1-methoxynaphthalene (**2**) was not a suitable photosensitizer, due to the intense absorption band exhibited by *trans*-*p*-cyanostilbene at the excitation wavelength of 308 nm (Figure 3).

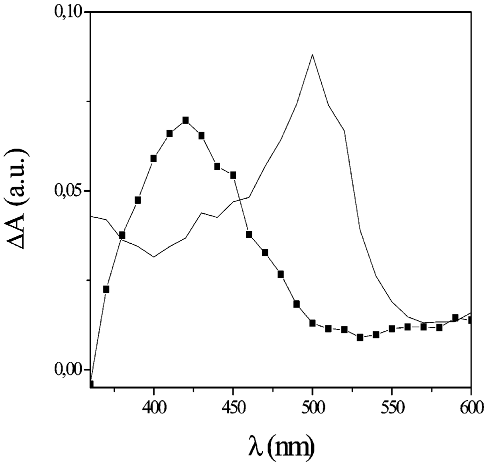

FIGURE 2. Transient absorption spectra obtained upon LFP (λ = 308 nm) of **2** (10^{-4} M), in acetonitrile, under argon: in the absence of quencher (■) and in the presence of 1.43×10^{-3} M of **1** (−). Spectra recorded 1 μs after the laser pulse.

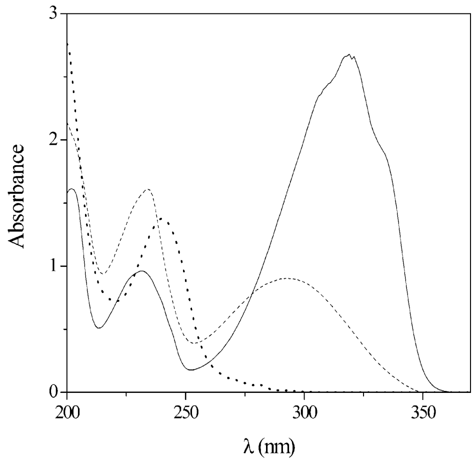

FIGURE 3. UV−vis absorption spectra of **1** (····), **3a** (−), and **3b** (- - -) in acetonitrile at 7.14×10^{-5} M.

Hence, 2,6-dimethoxynaphthalene (DMN) was chosen as an alternative photosensitizer, as it absorbs at significantly longer wavelengths and can be selectively excited at 355 nm. As a matter of fact, the transient species obtained upon 355 nm LFP of DMN in the presence of **3a** (Figure 4A) was similar to the intermediate formed upon the PET CR of oxetane **1**. Both species presented similar absorption bands with maxima around 500 nm and decayed with comparable kinetics (Figure 4B). By contrast, when *cis*-*p*-cyanostilbene (**3b**) was submitted to LFP in the presence of DMN, under identical conditions, a broader band with a higher absorption beyond 540 nm was obtained, attributable to the corresponding radical anion **3b**$^{\bullet-}$ (Figure 4A); its decay was slower than that of **3a**$^{\bullet-}$ (Figure 4B). From the spectral evolution of **3a**$^{\bullet-}$ and **3b**$^{\bullet-}$ with time, it is clear that no appreciable interconversion occurs; thus, trans−cis isomerization does not appear to take place at the radical anion stage.

These results allow to conclude that the primary process in the CR of **1** photosensitized by **2** is formation of **3a** via its radical anion. The extensive isomerization to the cis isomer **3b** is not a PET reaction; it simply

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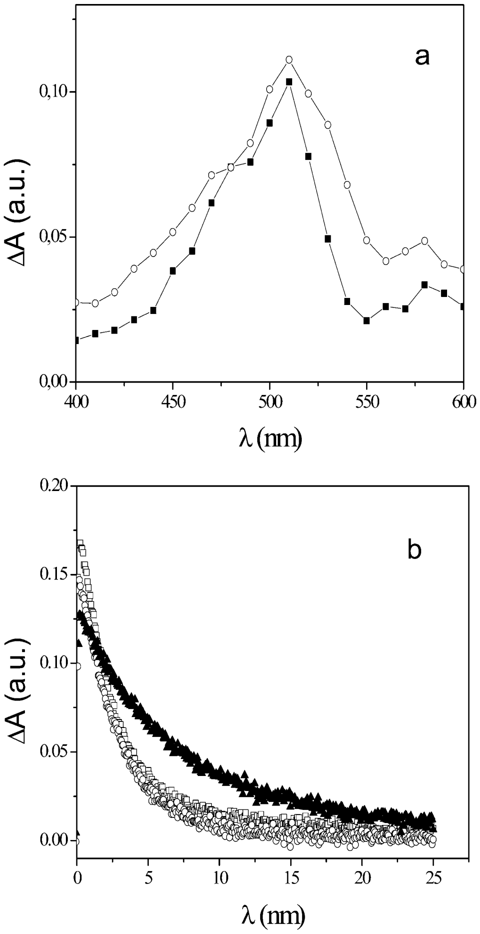

FIGURE 4. (a) Transient absorption spectra obtained upon LFP ($\lambda = 355$ nm) of DMN (8.5×10^{-4} M), in acetonitrile, under argon, in the presence of 1.43×10^{-3} M **3a** (■) and **3b** (○). Spectra recorded at 0.4 μs after the laser pulse. (b) Decay traces of the transient absorption at 510 nm in the presence of 1.43×10^{-3} M **1** (□), **3a** (○), and **3b** (▲).

reflects the fact that, at the wavelength employed for the preparative irradiations (300 nm), the molar absorption coefficient of **3a** is much higher than that of **3b** (see Figure 3). As a consequence, photoequilibrium mixtures overwhelmingly enriched in *cis*-*p*-cyanostilbene (**3b**) are obtained.

As stated above, significant amounts of triplet **2** are formed in the presence of concentrated oxetane, despite the efficient fluorescence quenching. Then, the question arises whether the triplet could be involved in the electron-transfer process, what would require as a first condition the existence of observable quenching of triplet **2** by **1**. Indeed, such triplet quenching did actually occur. The corresponding rate constant $k_q(T_1)$ was determined from the decay traces obtained for the T−T absorption of **2** in the presence of increasing amounts of **1** (Figure 5). By plotting the reciprocal lifetimes ($1/\tau$) against the concentration of oxetane, a linear relationship was obtained (see insert of Figure 5). The slopes of the straight lines correspond to $k_q(T_1)$ according to eq 5.

$$1/\tau = k_0 + k_q(T_1)[\text{oxetane}] \qquad (5)$$

Operating in this way, the value obtained for the triplet quenching rate constant was $k_q(T_1) = 4.9 \times 10^7$ M^{-1} s^{-1}.

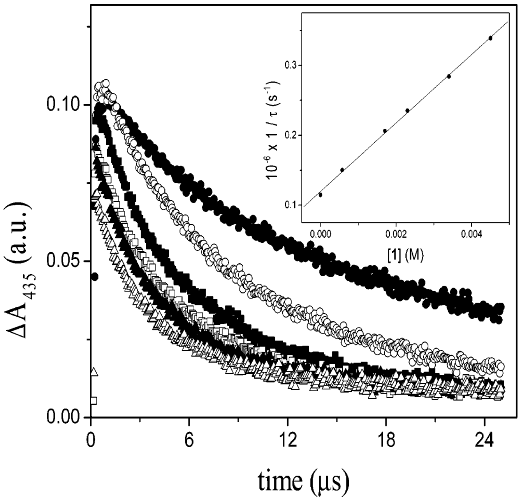

FIGURE 5. Decay traces of the T−T absorption of **2** (10^{-4} M) measured at 435 nm in the presence of increasing amounts of **1**: 0 M (●), 5.7×10^{-4} M (○), 1.7×10^{-3} M (■), 2.3×10^{-3} M (□), 3.4×10^{-3} M (▲), 4.5×10^{-3} M (△). Inset: Plot of $1/\tau$ against concentration of **1** to obtain $k_q(T_1)$.

Singlet vs Triplet Electron Transfer. The free energy changes associated with electron transfer from both the singlet and the triplet excited state were estimated using the Weller[20] equation (eq 6):

$$\Delta G_{ET}\,(\text{kcal/mol}) = 23.06[E_{D^{\bullet+}/D} - E_{A/A^{\bullet-}}] - E^*(S_1 \text{ or } T_1) \qquad (6)$$

The reduction potential, $E_{A/A^{\bullet-}}$, of **1** was measured by cyclic voltammetry in acetonitrile, under argon. Its experimental value after the first scan was −1.52 V vs SCE. The oxidation potential ($E_{D^{\bullet+}/D}$) of **2** as well as its singlet and triplet energies E^* (S_1 or T_1) have been previously measured.[21,22] Their corresponding values are 1.38 V vs SCE, 89.3 and 59.8 kcal/mol. Therefore, the $\Delta G_{ET}(S_1)$ and $\Delta G_{ET}(T_1)$ values were estimated by fitting the above data into eq 6; they were found to be −22.4 kcal/mol and +7 kcal/mol, respectively. Hence, PET from the singlet excited state would be an exergonic process, while the mechanism from the triplet excited state does not appear to be thermodynamically feasible.

Steady-State and Time-Resolved Studies in the Presence of Competing Quenchers. To establish in an unambiguous way the nature of the excited state of **2** involved in the CR of **1**, additional experiments were performed in the presence of competing quenchers such as oxygen and 1,3-cyclohexadiene (CHD). Both O_2 and CHD were found to quench the fluorescence of **2**, though with different rate constants. Figure 6 shows the two Stern−Volmer plots; from the linear relationships K_{SV} were found to be 446 M^{-1} (O_2) and 11.9 M^{-1} (CHD). Then, the corresponding $k_q(S_1)$ values were 3.3×10^{10} M^{-1} s^{-1} and 8.2×10^8 M^{-1} s^{-1}, respectively.

On the other hand, the triplet excited state of **2** was also quenched by O_2 and CHD with nearly diffusion-

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TABLE 1. Relative Contribution of the Different Pathways Resulting in Deactivation of Both the Singlet and Triplet Excited State of 2 by 1, O_2 and CHD, Together with the Relative CR Efficiencies[a]

		singlet quenching				triplet quenching			
	F^b	$Q(\mathbf{1})^c$	$Q(O_2)^c$	$Q(\mathrm{CHD})^c$	ISC[d]	$T(\mathbf{1})^e$	$T(O_2)^e$	$T(\mathrm{CHD})^e$	CR[f]
1	18	50			32	28			100
1 + CHD	17	48		5	30			30	90
1 + O_2	6	17	67		10		10		33

[a] Experimental conditions: **1** and CHD, 10^{-2} M; O_2, 9.1×10^{-3} M; **2**, 10^{-3} M; solvent, acetonitrile. [b] Fluorescence. [c] Fluorescence quenching. [d] Intersystem crossing. [e] Triplet quenching. [f] Relative CR efficience. All values are given in percent.

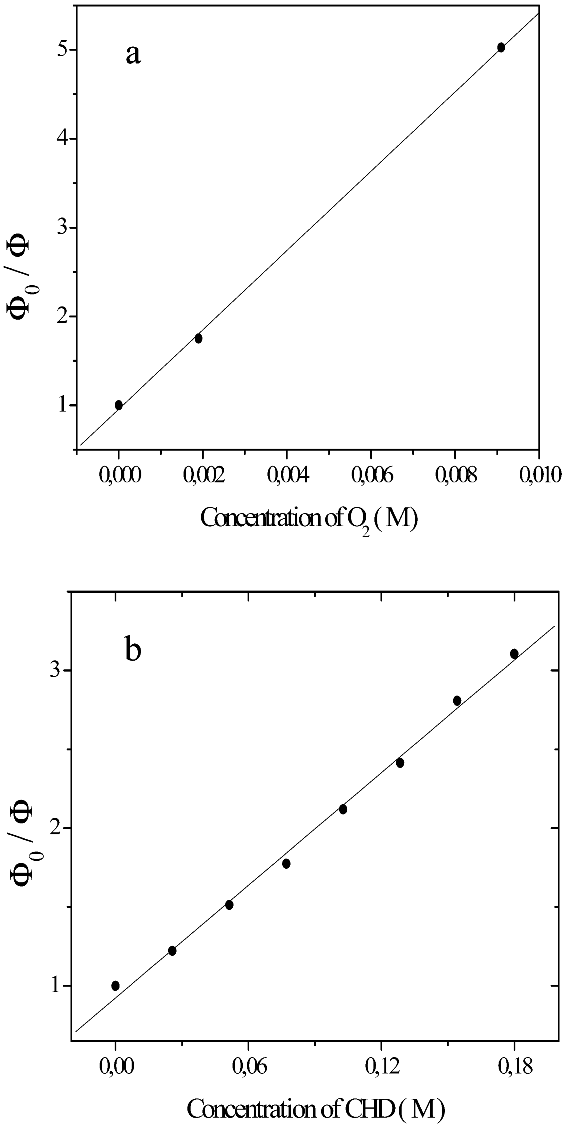

FIGURE 6. Stern–Volmer plot for the quenching of fluorescence of **2** in the presence of increasing amounts of (a) O_2 and (b) CHD to obtain the $k_q(S_1)$ values.

controlled rate ($k_q(T_1)$ ca. 5×10^{10} M^{-1} s^{-1} in the two cases). For example, the decay traces for the T–T absorption in the presence of increasing amounts of CHD are shown in Figure 7A, while the linear relationships between the reciprocal triplet lifetimes and the CHD concentrations are given in Figure 7B.

Therefore, the relative contributions of the different pathways resulting in the deactivation of the singlet and triplet excited state of **2** in the presence of **1**, O_2, and CHD were determined. This was done taking into account the above values of k_f, k_{isc}, $k_q(S_1)$, and $k_q(T_1)$, as well as the quencher concentration. As shown in Table 1, addition of 10^{-2} M CHD does not produce significant quenching of the fluorescence of **2**.

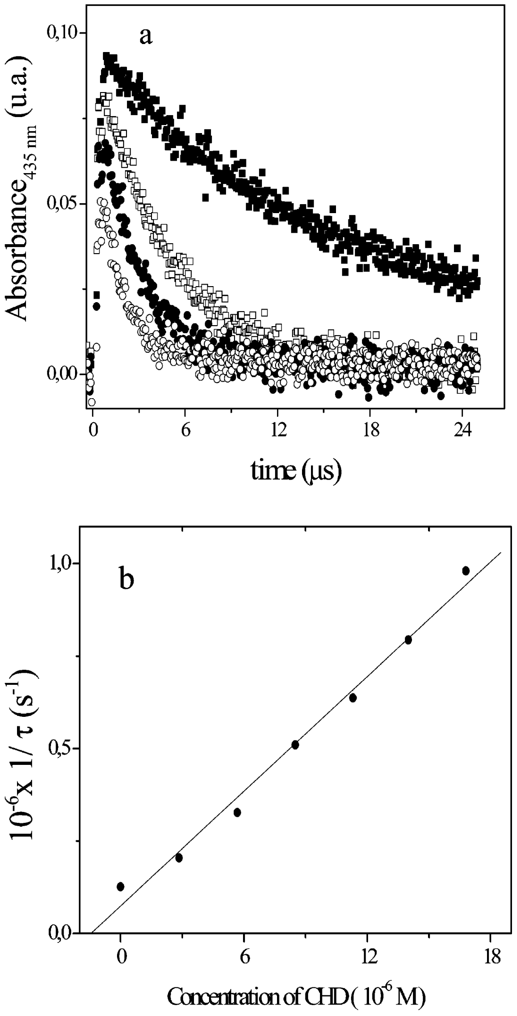

FIGURE 7. (a) Decay traces of the T–T absorption of **2** (10^{-4} M) measured at 435 nm, under argon, in the presence of increasing amounts of CHD: 0 M (■), 2.85×10^{-6} M (□), 5.68×10^{-6} M (●), 1.4×10^{-5} M (○). (b) Linear relationship to obtain $k_q(T_1)$.

Under these conditions, reaction of the singlet excited state of **2** with oxetane **1** still continues to be the major singlet deactivation pathway. By contrast, quenching of triplet **2** (which is formed in nearly the same amounts) by CHD competes favorably with that by **1**, providing the major triplet deactivation pathway. Thus, inhibition of the CR of **1** by addition of CHD would be an excellent probe for the involvement of the triplet excited state of the photosensitizer in the process.

On the other hand, dissolved O_2 appears to be a suitable quencher of both the singlet and triplet excited states of **2**. This is clear from the data of Table 1, following the same reasoning as above. Thus, combined preparative experiments using both CHD and O_2 as quenchers should allow to draw clear conclusions concerning the multiplicity of the photosensitizer excited-state involved in the PET CR of oxetane **1**.

Accordingly, mixtures of **1** (10^{-2} M) and **2** (10^{-3} M) were irradiated in the presence of either CHD (10^{-2} M) or O_2 (9.1×10^{-3} M) at the same concentrations used for the quenching experiments. The results are also given in Table 1. The small effect produced by CHD, together with the clear inhibition produced by O_2, allows to conclude that the reaction takes place from the singlet excited state of **2**.

Conclusions

Unambiguous experimental evidence has been obtained supporting that the reductive PET cycloreversion of oxetane **1** mediated by 1-methoxynaphthalene takes place from the singlet excited state of the photosensitizer. By contrast with the regioselectivity previously observed for the analogous reaction of thymine-derived oxetanes, splitting of **1** occurs with cleavage of the O−C_2 and C_3−C_4 bonds, leading to products different from the reagents used in the Paterno−Büchi synthesis. Finally, the radical anion of *p*-cyanostilbene is observed, instead of the radical anion of the carbonyl fragment.

Experimental Section

Chemicals. 1-Methoxynaphthalene (**2**) and 2,6-dimethoxynaphthalene (DMN) were commercially available. Oxetane **1** was prepared via Paterno−Büchi photocycloaddition of 4-cyanobenzaldehyde and *trans*-β-methylstyrene.[11] Compounds **3a** and **3b** were synthesized as previously described, by following the modified Wittig−Horner reaction.[23]

Cycloreversion Reaction. A solution of oxetane **1** (10^{-2} M) with photosensitizer **2** (10^{-3} M) in CH_3CN (2 mL) was placed in a quartz tube and bubbled with argon. Then, the solution was irradiated during 30 min in a multilamp photoreactor, using 8 W lamps (4×) with emission maximum at $\lambda_{max} = 300$ nm. The reaction was followed by GC−MS and ^1H NMR spectroscopy. Control experiments showed that CR does not take place in the dark or in the absence of photosensitizer.

Cyclic Voltammetry. The redox potentials were measured by cyclic voltammetry. All measurements were made in acetonitrile containing tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte, using a glassy carbon working electrode and ferrocene in acetonitrile (5 mg in 30 mL) as standard, $E_{pa} = 423$ mV and $E_{pc} = 345$ mV. The scan rate was 400 mV/s. Potentials are reported with respect to the saturated calomel electrode (SCE) as reference.

Fluorescence Spectroscopy. The steady-state fluorescence spectra were obtained with a FS 900 spectrofluorimeter equipped with a 450 W xenon lamp. The samples were placed into quartz cells of 1 cm path length. 1-Methoxynaphthalene concentration was fixed adjusting the absorbance of the solution at an arbitrary value between 0.2 and 0.3.

Time-Resolved Absorption Spectroscopy. The laser flash photolysis system was based on a pulsed XeCl Excimer Laser, using 308 nm as excitation wavelength. The single pulses were ca. 17 ns duration and the energy was ca. 100 mJ/pulse. A Lo255 Oriel xenon lamp was employed as detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a monochromator, a photomultiplier (PMT) system, and an oscilloscope. The output signal from the oscilloscope was transferred to a personal computer for study.

Acknowledgment. Financial support by the MCYT (Grant No. BQU2001-2725) is gratefully acknowledged.

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