Involvement of Triplet Excited States and Olefin Radical Cations in Electron-Transfer Cycloreversion of Four-Membered Ring Compounds Photosensitized by (Thia)pyrylium Salts

Miguel A. Miranda,* M. Angeles Izquierdo, and Francisco Galindo

Departamento de Química, Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Camino Vera s/n, Apartado 22012, 46022 Valencia, Spain

mmiranda@qim.upv.es

Received November 26, 2001

Cycloreversion of 1,2,3,4-tetraphenylcyclobutanes **1a,b** and oxetane **2** is achieved using (thia)pyrylium salts as electron-transfer photosensitizers. Radical cation intermediates involved in the electron-transfer process have been detected using laser flash photolysis. The experimental results are consistent with the reaction taking place from the triplet excited state of the sensitizer.

Introduction

Cycloreversion (CR) of four-membered ring compounds is one of the most important electron-transfer (ET)catalyzed pericyclic reactions.¹ It has attracted much attention in recent years, mainly focused on theoretical calculations about the reaction pathways, stereoelectronic effects, and biological implications in DNA repair.^{1–11}

Recent theoretical studies on the CR of cyclobutane radical cations have established that the reaction pro-

(2) (a) Wiest, O. J. Phys. Chem. A **1999**, 103, 7907–7911. (b) Jungwirth, P.; Carsky, P.; Bally, T. J. Am. Chem. Soc. **1993**, 115, 5776–5782. (c) Jungwirth, P.; Bally, T. J. Am. Chem. Soc. **1993**, 115, 5783–5789.

(3) (a) Aida, M.; Inoue, F.; Kaneko, M.; Dupuis, M. J. Am. Chem. Soc. **1997**, *119*, 12274–12279. (b) Rak, J.; Voityuk, A. A.; Rösch, N. J. Phys. Chem. A **1998**, *102*, 7168–7175.

(4) Wang, Y.; Gaspar, P. P.; Taylor, J. S. J. Am. Chem. Soc. 2000, 122, 5510–5519.

(5) (a) Moriarty, R. M. Top. Stereochem. 1974, 8, 271-421. (b) Hoffmann, R.; Davidson, R. B. J. Am. Chem. Soc. 1971, 93, 5699-5705. (c) Shima, K.; Kimura, J.; Yoshida, K.; Yasuda, M.; Imada, K.; Pac, C. Bull. Chem. Soc. Jpn. 1989, 62, 1934-1942. (d) Pac, C.; Go-An, K.; Yanagida, S. Bull. Chem. Soc. Jpn. 1989, 62, 1951-1959. (e) Majima, T.; Pac, C.; Sakurai, H. J. Am. Chem. Soc. 1980, 102, 5265-5273. (f) Pac, C. Pure Appl. Chem. 1986, 58, 1249-1256. (g) Yamashita, Y.; Yagashi, H.; Mukai, T. Tetrahedron Lett. 1985, 30, 3579-3582.

(6) (a) Yamashita, Y.; Ikeda, H.; Mukai, T. J. Am. Chem. Soc. 1987, 109, 6682–6687. (b) Okada, K.; Hisamitsu, K.; Miyashi, T.; Mukai, T. J. Chem. Soc., Chem. Commun. 1982, 974–976. (c) Okada, K.;

Hisamitsu, K.; Mukai, T. *Tetrahedron Lett.* **1981**, *22*, 1251–1254. (7) (a) Kaupp, G. *Angew. Chem.* **1974**, *84*, 741–742. (b) Kaupp, G.; Stark, M. *Chem. Ber.* **1977**, *110*, 3084–3110.

(8) (a) Heelis, P. F.; Hartman, R. F.; Rose, S. D. Chem. Soc. Rev. **1995**, 24, 289–297. (b) Sancar, A. Mutat. Res. **1990**, 236, 147–160. (c) Cadet. J.; Vigny, P. In Bioorganic Photochemistry; Morrison, H., Ed.; Wiley: New York, 1990; pp 1–272. (d) Fisher, G. J.; Johns, H. E. In Photochemistry and Photobiology of Nucleic Acids; Wang, S. Y., Ed.; Academic Press: New York, 1976; pp 225–294.

Academic Press: New York, 1976; pp 225–294.
(9) (a) Prakash, G.; Falvey D. E. J. Am. Chem. Soc. 1995, 117, 11375–11376. (b) Kim, S. T.; Malhotra, K.; Smith, C. A.; Taylor, J. S.; Sancar, A. J. Biol. Chem. 1994, 269, 8535–8540. (c) Zhao, X.; Liu, J.; Hsu, D. S.; Zhao, S.; Taylor, J. S.; Sancar, A. J. Biol. Chem. 1997, 272, 32580–32590.

(10) (a) Heelis, P. F.; Hartman, R. F.; Rose, S. D. J. Photochem. Photobiol., A 1996, 95, 89–98. (b) Scannell, M. P.; Fenick, D. J.; Yeh, S. R.; Falvey, D. E. J. Am. Chem. Soc. 1997, 119, 1971–1977. (c) Yeh, S. R.; Falvey, D. E. J. Am. Chem. Soc. 1991, 113, 8557–8558. ceeds in a concerted fashion.² However, substituents on the cyclobutane ring may alter the mechanism by stabilization of an acyclic intermediate on a very flat energy hypersurface.³ In the case of oxetanes, semiempirical calculations have shown that CR of their radical cations is an exothermic and stepwise reaction.⁴

Stereoelectronic effects are of significance for exploring the reactivity of these rigid systems.^{5,6} One of the most important features is the *cis* effect of aryl substituents, which can be subjected to electronic coupling through the ring σ orbitals.⁷ This results in weaker σ bonds and directs the splitting mode.

The ET-photosensitized CR of cyclobutanes and oxetanes is of high biological interest because of its involvement in DNA repair. Thus, CR of cyclobutane pyrimidine dimers should be achieved in the repair of UV-damaged DNA.⁸ Also, CR of oxetanes appears to be involved in the photoenzymatic repair of the (6–4) photoproducts of the DNA dipyrimidine sites by photolyase.⁹ Although photoreducing sensitization is the mode usually operating in biological systems,¹⁰ the photooxidative approach is considered to be relevant for DNA repair therapies.¹¹

Despite the considerable interest of ET-photosensitized oxidative CR of cyclobutanes and oxetanes, some fundamental aspects require further studies. These include (i) detection of transient intermediates by means of timeresolved techniques and (ii) influence of the excited-state multiplicity (singlet vs triplet) on the fate of the reaction.

For instance, 1,2,3,4-tetraphenylcyclobutanes have been previously shown to produce two stilbene units upon direct irradiation¹² and γ radiolysis via radical cations;¹³ however, there is no report on their CR by irradiation in the presence of ET photosensitizers. This may be due to the high redox potentials of these cyclobutanes (ca. 2 V vs SCE; see below), which prevent their oxidation using most of the commonly employed photosensitizers.

^{*} To whom correspondence should be addressed. Phone: 963877340. Fax: 963879349.

^{(1) (}a) Mizuno, K.; Pac, C. In *CRC Handbook of Organic Photochemistry and Photobiology*, Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; pp 359–365. (b) Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer*, Elsevier: Amsterdam, Oxford, New York, Tokyo, 1988; Part A, pp 546–549.

^{(11) (}a) Dandliker, P. J.; Holmlin, R. E.; Barton, J. K. *Science* **1997**, *275*, 1465–1468. (b) Pac, C.; Miyamoto, I.; Masaki, Y.; Ferusho, S.; Yanagida, S.; Ohno, T.; Yoshimura, A. *Photochem. Photobiol.* **1990**, *52*, 973–979.

^{(12) (}a) Takamuku, S.; Beck, G.; Schnabel, W. *J. Photochem.* **1979**, *11*, 49–52. (b) Shizuka, H.; Seki, I.; Morita, T.; Iizuka, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2074–2078.

⁽¹³⁾ Tojo, S.; Morishima, K.; Ishida, A.; Majima, T.; Takamuku, S. Bull. Chem. Soc. Jpn. **1995**, *68*, 958–966.





In the case of oxetanes, a preliminary study using 2,2diaryl derivatives and cyanoaromatic compounds as ET partners has shown that the CR reaction occurs through the excited singlet state of the photosensitizer.¹⁴ Although the process was explained via formation of radical cations, no intermediate of this type was detected. Besides, CR ensues with cleavage of the same C–C bonds formed in the Paterno–Büchi photocycloaddition employed to synthesize the starting 2,2-diaryloxetanes. A radical chain mechanism has been found to operate when electron-donating substituents are attached to the aryl groups.

In the present work, the above points i and ii will be addressed by using 1,2,3,4-tetraphenylcyclobutanes **1a,b** and the diphenyl-substituted oxetane **2** as electron donors (Chart 1), together with a series of (thia)pyrylium salts **3a**-**d** as acceptors (Chart 2), to gain further insight into the mechanistic aspects of this reaction.

Pyrylium salts are a potentially useful group of photosensitizers.¹⁵ They are extremely good photooxidizing agents and can be selectively excited because of their absorption in the visible. On the other hand, depending on the substitution pattern and the reaction conditions, they can generate radical ion pairs of different multiplicities (singlet or triplet)¹⁶ and hence may be of interest to study the influence of this factor on the reaction, for instance regarding the splitting mode and the stereoselectivity of the products.

Results and Discussion

Steady-State Photolysis. Irradiation of cyclobutanes **1a,b** was carried out in the presence of catalytic amounts



Table 1. Cycloreversion Quantum Yields^a

	$\phi_{\rm CR}(\mathbf{1a})$		$\phi_{ m CF}$	e(1b)	$\phi_{\rm CR}(2)$		
\mathbf{S}^{b}	argon	oxygen	argon	oxygen	argon	oxygen	
3a	0.10	0.06	0.02	0.003	0.02	_	
3b	0.50	0.11	0.09	0.02	0.10	_	
3c	0.40	0.10	0.13	0.01	0.04	_	
3d	-	_	-	_	-	-	

^{*a*} Experimental conditions: **1a**, **1b**, **2**, 10^{-4} M; sensitizers **3a**-**d**, 2.5×10^{-5} M; solvent, acetonitrile; 450 W xenon lamp, monochromatic light of $\lambda = 420$ nm; actinometer, potassium ferrioxalate. The solutions were placed in sealed cuvettes and bubbled with argon/oxygen for 15 min. ^{*b*} S = sensitizer.

of sensitizers 3a-d. In all cases except for 3d, *trans*stilbene 4 was detected as the only photoproduct by direct GC-MS and ¹H NMR analysis of the reaction mixtures. When oxetane 2 was irradiated under the same conditions, CR led to formation of *trans*-stilbene and acetaldehyde as the only photoproducts (Scheme 1).

To obtain reliable quantitative data, the CR quantum yields (ϕ_{CR}) were measured using potassium ferrioxalate as actinometer, under both oxygen and argon. The results are shown in Table 1.

These results clearly show that (a) the CR reaction is photosensitized by pyrylium salts, and the extent of the reaction clearly depends on the nature of the employed salt, (b) in the case of oxetane **2**, CR produces carbonyl and olefin units different from the reagents employed in the Paterno–Büchi cycloaddition, (c) the most efficient photosensitizer is the thiapyrylium salt **3b**, while the methoxy derivative **3d** is unreactive, and (d) the reaction is clearly quenched by oxygen. Moreover, the fact that the obtained quantum yields were much less than unity appears to rule out the possibility of a chain reaction.

Laser Flash Photolysis Studies of Cyclobutanes 1a,b. To gain further insight into the mechanism of the observed cycloreversion, laser flash photolysis (LFP) experiments were conducted under different experimental conditions.

Working with low cyclobutane concentrations (ca. 10^{-4} M), irradiation of deoxygenated acetonitrile solutions of cyclobutane **1a** in the presence of **3a**–**c** (excitation at λ = 355 nm) gave rise to an intense signal centered around 470 nm, which was assigned to the radical cation **4**⁺⁺ on the basis of literature data^{16,17} (Figure 1). It was formed "instantaneously" (i.e., its growth was not observable within our time scale) and exhibited a monoexponential decay with τ = 11.53 μ s (see the inset of Figure 1).

 ⁽¹⁴⁾ Nakabayashi, K.; Kojima, J. I.; Tanabe, K.; Yasuda, M.; Shima,
 K. Bull. Chem. Soc. Jpn. 1989, 62, 96–101.

^{(15) (}a) Miranda, M. A.; García, H. Chem. Rev. 1994, 94, 1063–1089. (b) Corma, A.; Fornés, V.; García, H.; Miranda, M. A.; Primo, J.; Sabater, M. J. J. Am. Chem. Soc. 1994, 116, 9767–9768. (c) Galindo, F.; Miranda, M. A. J. Photochem. Photobiol., A 1998, 113, 155–161. (d) Martiny, M.; Steckhan, E.; Esch, T. Chem. Ber. 1993, 126, 1671–1682. (e) Akaba, R.; Arai, S., Sakuragi, H.; Tokumaru, K. J. Chem. Soc., Chem. Commun. 1987, 1262–1263.

^{(16) (}a) Miranda, M. A.; Izquierdo, M. A.; Galindo, F. *Org. Lett.* **2001**, *3*, 1965–1967. (b) Akaba, R.; Oshima, K.; Kawai, Y.; Obuchi, Y.; Negishi, A.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1991**, *32*, 109–112. (c) Kuriyama, Y.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1988**, 1193–1196. (d) Akaba, R.; Kamata, M.; Koike, A.; Mogi, K. E.; Kuriyama, Y.; Sakuragi, H. *J. Phys. Org. Chem.* **1997**, *10*, 861–869.

^{(17) (}a) Shida, T. *Electronic Absortion Spectra of Radical Ions*; Elsevier: Amsterdam, 1988; p 113. (b) Hamil, W. H. In *Radical Ions*; Kaiser, E. T., Kevan, L., Eds.; Interscience: New York, 1968; p 399.



Figure 1. Transient spectrum obtained from LFP ($\lambda = 355$ nm) of **1a** (1.4×10^{-4} M) and **3a** (1.2×10^{-4} M) in acetonitrile, under nitrogen. Spectrum recorded 10 μ s after the laser pulse. Inset: rise time and decay of the signal peaking at 470 nm.

Besides the intense band at 470 nm, a smaller one at 550 nm was also clearly distinguished; the latter was safely assigned to 2,4,6-triphenylpyranyl radical, the reduced species of **3a**.¹⁸ Analogous results were obtained using 3b and 3c as photosensitizers; by contrast, no transient spectrum was obtained in the case of 3d. On the other hand, LFP of solutions of the all-trans dimer **1b** in the presence of $3\mathbf{a} - \mathbf{c}$ also gave rise to a band at 470 nm assigned to radical cation 4⁺⁺. Again, pyrylium salt 3d gave no measurable signal. On the basis of the results obtained in the above time-resolved experiments, CR of **1a**,**b** follows an ET mechanism where ring splitting at low substrate concentrations gives rise to the radical cation of trans-stilbene as the only detectable intermediate. Although in principle the isomeric radical cation of cis-stilbene could also be formed, the absence of its characteristic transient absorption at 515 nm allows this possibility to be ruled out.^{16c}

Slightly different shapes and positions of the bands were observed at higher concentrations of cyclobutane **1b** (ca. 10^{-2} M), especially considering the evolution with time. While in the case of 1a decay of the 470 nm band was uniform (Figure 2, bottom), the absorption band generated from 1b changed its shape as it decayed (Figure 2, top). This is indicative of the presence of at least two species: $2 \mu s$ after the pulse the maximum is located at 470 nm, which could be associated with 4^{•+}, but 3 μ s later the maximum is clearly shifted to 460 nm. As a matter of fact, analysis of the decay at 470 nm shows two distinct components. The species with a longer lifetime could be attributed to a complex between 4 and **4**^{•+}. Actually, when concentrated (10^{-2} M) acetonitrile solutions of 4 were submitted to LFP, the peaks at 470 and 460 nm were clearly observed. By contrast, only the peak at 470 nm was detected when more diluted solutions of 4 were employed.

Similar dimeric complexes have been previously postulated^{19a} in the LFP of stilbenes in the presence of pyrylium salts. Likewise, pulse radiolysis experiments with stilbene^{19b-d} and 1,2,3,4-tetraphenylcyclobutanes¹³ have led to detection of related species assigned to dimeric radical cations.

The lack of such a signal at 460 nm in the irradiations of **1a** does not allow formation of $4/4^{++}$ complexes to be



Figure 2. Transient spectra obtained from LFP ($\lambda = 355$ nm) of **1a,b** (10^{-2} M) and **3b** (1.2×10^{-4} M) in acetonitrile, under nitrogen, recorded at different times after the laser pulse. Top: obtained for **1b**. Bottom: obtained for **1a**.

ruled out. Probably the lifetime of this intermediate is too short, and/or steric interactions lead rapidly to a complete bond rupture.⁵

Laser Flash Photolysis Studies of Oxetane 2. In a typical experiment, LFP (355 nm) of a mixture of **2** and **3b** in acetonitrile gave a transient with an absorption maximum at 470 nm (Figure 3), which can be ascribed to the radical cation of *trans*-stilbene on the basis of literature data.^{16,17}

This confirmed that photocycloreversion of **2** follows an electron-transfer mechanism and indicated that splitting of the oxetane gives rise to the radical cation of *trans*-stilbene instead of the radical cation of 1-phenylpropene.

Thermodynamic Analysis of the Electron-Transfer Reaction. In principle the PET process might involve either the excited singlet or the excited triplet of the pyrylium salt. To check the feasibility of the two pathways, the free energy change associated with electron

⁽¹⁸⁾ Pragst, F. Electrochim. Acta 1976, 21, 497-500.

^{(19) (}a) Spada, L. T.; Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.;
Elbert, J. E., Gould, I. R.; Farid, S. J. Am. Chem. Soc. 1990, 112, 8055–8064. (b) Akaba, R.; Sakuragi, H.; Tokumaru, K. Chem. Phys. Lett.
1990, 174, 80–84. (c) Majima, T.; Tojo, S.; Ishida, A.; Takamuku, S. J. Phys. Chem. 1996, 100, 13615–13625. (d) Majima, T.; Tojo, S.; Ishida, A.; Takamuku, S. J. Org. Chem. 1996, 61, 7793–7800. (e) Kuriyama, Y.; Sakuragi, H.; Tokumaru, K.; Yoshida, Y.; Tagawa, S. Bull. Chem. Soc. Jpn. 1993, 66, 1852–1855.



Figure 3. Transient spectra obtained from LFP ($\lambda = 355$ nm) of **2** (1.2 × 10⁻⁴ M) and **3b** (10⁻⁴ M) in acetonitrile, under argon.

Table 2. Thermodynamics of the PhotosensitizedET-reaction

					-					
				$\Delta G_{ m S}^{ m c}$			$\Delta G_{\mathrm{T}}^{\mathrm{c}}$			
\mathbf{S}^{a}	$E_S{^{b,c}} \\$	$E_{T}{}^{b,c} \\$	1a	1b	2	1a	1b	2		
3a	66	53^d	-13	-13	-24	-0.7	-0.2	-11		
3b	66	52^d	-15	-15	-26	-1.5	-1.0	-12		
3c	63	na ^e	-13	-13	-25	na ^e	na ^e	na ^e		
3d	58	51^d	+0.1	+0.1	11	+6.7	+7.1	-4		

 $^a \rm S$ = sensitizer. $^b E_{\rm S}$ = singlet energy, $E_{\rm T}$ = triplet energy. $^c \rm Given$ in kcal/mol. $^d \rm Taken$ from the literature. 21 $^e \rm na$ = not available.

transfer was calculated using the Weller²⁰ equation (eq 1) for both excited states.

$$\Delta G (\text{kcal/mol}) = 23.06[E_{\text{D}\bullet+/\text{D}} - E_{\text{A/A}\bullet-}] - E^*_{\text{A}}$$
 (1)

The $E_{D*^+/D}$ was measured by cyclic voltammetry in acetonitrile and was found to be 1.98 V vs SCE for **1a**, 2.00 V vs SCE for **1b**, and 1.42 V vs SCE for **2**. On the other hand, the $E_{A*^-/A}$ singlet and triplet energies of the sensitizers had been previously measured.^{15a,d,21} The ΔG values obtained by fitting the above data in eq 1 are given in Table 2. According to them, the reaction would be possible in all cases, although CR of cyclobutanes would be less favorable starting from triplet **3d**. Thus, the cycloreversion reaction might in principle occur from both excited states.

Fluorescence Quenching of the Pyrylium Salts. To gain further insight into the reaction mechanism, quenching of the pyrylium salt fluorescence by **1a,b** and **2** was investigated. The rate constants (k_q) were calculated using a Stern–Volmer analysis according to the equation $I_o/I = 1 + K_{sv}[Q]$, were $K_{sv} = k_q \tau$.

The results are shown in Table 3. From these data it is clear that fluorescence quenching occurs at a nearly diffusion controlled rate, except in the case of the methoxy derivative **3d** (Table 3).

Thus, according to the above photophysical data, the cycloreversion reaction might take place both for the singlet and for the triplet excited states; however, the fact that the pyrylium salt **3b**, with the highest intersystem crossing quantum yield, is the most efficient sensitizer points clearly to triplet involvement. A pro-

 Table 3. Deactivation Pathways for the Excited Singlet

 States of 3a-d

					$10^{-10} k_{ m q}^{d}$		
\mathbf{S}^{a}	$10^{-8}k_{\mathrm{f}}^{b}$	$ au_{\mathrm{f}}$ (ns)	$10^{-8}k_{\rm ISC}^{b}$	$\phi_{\rm ISC}{}^c$	1a	1b	2
3a	1.1	4.45	1.2	0.53	1.5	1.4	0.7
3b	0.1	4.41	2.1	0.94	1.2	0.8	0.7
3c	2.5	1.31	5.1	0.67	1.7	1.9	1.1
3d	1.8	5.52	<0.1	0.03	-	-	_

^{*a*} S = sensitizer. ^{*b*} Rate constants for fluorescence (k_f) or intersystem crossing (k_{ISC}) given in s⁻¹ (taken from the literature)^{15a,21} in the absence of quencher. ^{*c*} ϕ_{ISC} = intersystem crossing quantum yield, in acetonitrile as solvent. ^{*d*} Rate constant for fluorescence quenching (k_q) by **1a,b** and **2** given in s⁻¹ M⁻¹.



posed mechanism for the electron-transfer process is shown in Scheme 2.

This is also supported by the fact that the reaction is much less efficient in the presence of oxygen, a good triplet quencher. Also, the ϕ_{CR} lower than unity suggests that the reaction does not proceed through a radical chain mechanism as has been reported for analogous compounds.⁶

The last equation of Scheme 2 is back electron transfer from the reduced species of sensitizer $(3^{\bullet-})$ to $4^{\bullet+}$, leading to the neutral *trans*-stilbene.

To make sure that the triplets of $3\mathbf{a}-\mathbf{c}$ are formed in sufficient amount, even at high oxetane and cyclobutane concentrations, it appeared necessary to calculate the relative contributions of the different singlet deactivation pathways under the employed reaction conditions (Table 4). Calculations were performed taking into account the competition among fluorescence emission, fluorescence quenching, and intersystem crossing, governed by the respective rate constants and by the quencher concentration.

It is interesting that (thia)pyrylium salts **3b** and **3c** produce the highest amount of triplets at the two cyclobutane concentrations, followed by the parent compound **3a**. This correlates well with the relative CR efficiencies given in Table 1.

Experimental Section

Chemicals. Sensitizer **3a** was commercially available. Its analogue **3b** was synthesized according to the procedure

⁽²⁰⁾ Weller, A. Z. Phys. Chem. (Wiesbaden) 1982, 133, 93.

⁽²¹⁾ Searle, R.; Williams, J. L. R.; DeMeyer, D. E.; Doty, J. C. J. Chem. Soc., Chem. Commun. 1967, 22, 1165.

 Table 4.
 Relative Contribution of the Different

 Pathways Resulting in Deactivation of the Excited
 Singlet of 3a-d at Two Concentrations of Substrate^a

		F (%) ^c			ISC (%) ^d		
[1] or [2] (M)	\mathbf{S}^{b}	1a	1b	2	1a	1b	2
10^2	3a	29	30	36	31	33	41
	3b	3	4	5	63	70	72
	3c	27	26	29	55	54	59
	3d	97	97	97	3	3	3
10^{-4}	3a	48	46	46	50	52	53
	3b	5	5	6	94	95	93
	3c	33	33	33	67	67	66
	3d	97	97	97	3	3	3

^{*a*} The rest up to 100 corresponds to quenching of the fluorescence of **3a**–**d** by **1a,b** or **2**. ^{*b*} S = sensitizer. ^{*c*} F = fluorescence. ^{*d*} ISC = intersystem crossing.

described by Wizinger and Ulrich,²² while **3c,d** were obtained following the method described by Steckhan and co-workers.^{15d} Cyclobutanes **1a,b** were synthesized by photodimerization of stilbene.²³ Oxetane **2** was prepared via the Paterno–Büchi photocycloaddition of benzaldehyde and *trans-* β -methylstyrene.²⁴

All compounds were characterized by ${}^{1}H$ and ${}^{13}C$ NMR spectra, which were recorded on a 300 MHz spectrometer. Data were consistent with those found in the literature.

Cycloreversion Reactions. Solutions of cyclobutane **1a**,**b** and oxetane **2** (5×10^{-2} M) with sensitizer **3a**–**d** (10^{-3} M) in CDCl₃ (1 mL) were placed in NMR tubes and bubbled with argon. Then, cyclobutane solutions were irradiated for 1 h while oxetane solutions were irradiated for 20 min in a multilamp photoreactor, using 8 W lamps ($4 \times$) with emission maximum at 300 nm and using a filter to select $\lambda > 340$ nm. The reaction was followed by ¹H NMR, which was recorded before and after the irradiation. Control experiments showed that photocycloreversion does not take place in the dark or in the absence of photosensitizer. In the case of **1a**,**b** the reaction was also followed by GC and GC–MS.

Cycloreversion Quantum Yields. Acetonitrile solutions of cyclobutane **1a,b** and oxetane **2** (10^{-4} M) with sensitizer **3a-d** (2.5×10^{-5} M) were placed in sealed cuvettes and bubbled with argon/oxygen for 15 min. Samples were irradiated by means of a xenon 450 W lamp, isolating the $\lambda = 420$ nm line by means of a monochromator, to ensure that the

sensitizer was the only absorbing species. Potassium ferrioxalate was employed as actinometer.²⁵ The CR quantum yields were calculated following the increase in the absorbance at 300 nm associated with the formation of *trans*-stilbene.

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 in quartz cells of 1 cm path length. The pyrylium salt concentration was fixed, adjusting the absorbance of the solutions at arbitrary concentration between 0.1 and 0.3.

Time-Resolved Absorption Spectroscopy. The laser flash photolysis system was based on a pulsed Nd:YAG laser, using 355 nm as the excitation wavelength. The single pulses were of ca. 10 ns duration, and the energy was ca. 20 mJ/pulse. A xenon lamp was employed as the detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the xenon lamp, a monochromator, a photomultiplier (PMT) system made up of a side-on PMT tube, PMT housing, and a PMT power supply. The output signal from the oscilloscope was transferred to a personal computer for study.

Conclusions

In summary, electron-transfer CR of cyclobutanes **1a**,**b** and oxetane **2** can be achieved by photosensitization with triaryl (thia)pyrylium salts. The reaction takes place from the excited triplet state of the photosensitizer, as indicated by quenching by molecular oxygen and by the negative (or slightly positive) values of ΔG from this state. It ensues with splitting into *trans*-stilbene radical cation and neutral *trans*-stilbene in the case of cyclobutanes **1a**,**b** or acetaldehyde plus *trans*-stilbene radical cation for oxetane **2**. *trans*-Stilbene radical cation has been detected as an intermediate of the reaction by means of laser flash photolysis. Further studies are in progress to check the scope, limitations, and potential synthetic interest of this reaction.

Acknowledgment. Financial support by the Spanish Ministerio de Ciencia y Tecnologia, Grant PB 97 0339, is gratefully acknowledged.

JO011103I

⁽²²⁾ Wizinger, R.; Ulrich, P. *Helv. Chim. Acta* 1956, *39*, 1–4.
(23) Shechter, H.; Link, W. J.; Tiers, G. V. D. *J. Am. Chem. Soc.* 1963, *85*, 1601–1605.

⁽²⁴⁾ Fleming, S. A.; Gao, J. J. Tetrahedron Lett. 1997, 38, 5407-541.

^{(25) (}a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536. (b) Braun, A. M.; Maurette, M. T.; Oliveros, E. *Technologie Photochimique*; Presses Polytechniques Romandes: Lausanne, Switzerland, 1986; p 62.