Electron-Transfer Cycloreversion of 2,3-Diaryloxetanes: Influence of the Substitution and the Photosensitizer on the Regioselectivity

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The regioselectivity in the oxidative electron-transfer cycloreversion (CR) of 2,3-diaryloxetanes depends on the substitution of the aryl groups and on the nature of the electron-transfer photosensitizer. The reaction occurs with fragmentation of the C2–C3 and C4–O bonds either in the presence of electron-releasing substituents in the 3-aryl groups, or when chloranil is used as photosensitizer. Thus, CR of the methoxy-substituted derivative *trans*,*trans*-3-(4-methoxyphenyl)-4-methyl-2-phenyloxetane (**1b**) results in the production of *trans*-anethole and benzaldehyde. In this case, the *trans*-anethole radical cation has been detected as transient intermediate by means of laser flash photolysis. Likewise, CR of **1a**, photosensitized by chloranil, results in the formation of products arising from the trapping of the *trans*-β-methylstyrene radical cation by chloranil-derived intermediates. The reverse regioselectivity has been previously found in the ET cycloreversion of 4-methyl-2,3-diphenyloxetane (**1a**) using (thio)pyrylium salts as photosensitizers.

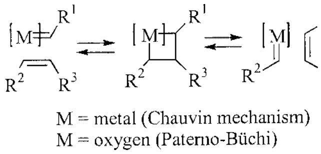
Introduction

Carbon−carbon bond breaking involving radical cations has been studied in a number of organic compounds containing strained rings, such as cyclopropanes, oxiranes, cyclobutanes and spiroalkanes.[1] Trapping of the ring-opened distonic radical cations with nucleophiles, electron-rich olefins, NO or oxygen may have interesting synthetic applications.[2] However, there are very few literature reports describing the cycloreversion (CR) of oxetanes under oxidative electron-transfer (ET) conditions.[3,4]

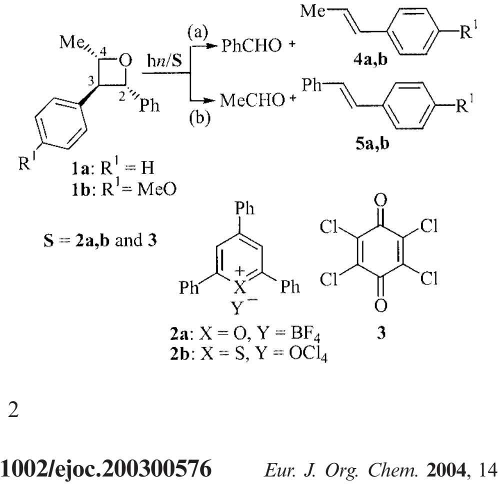
Oxetanes can be easily obtained by the photocycloaddition of carbonyl compounds to alkenes (Paterno−Büchi reaction).[5] Their CR involves cleavage of two bonds (C−C and C−O) and can yield formal olefin metathesis products. In this context, the CR of oxetanes presents clear analogies with the Chauvin mechanism involved in the interconversion of olefins and (alkylidene)metal compounds through the intermediacy of metallacyclobutanes (Scheme 1).[6,7] Ring-splitting of oxetanes can be achieved by chemical means[8] (hydrogenolysis or nucleophilic attack), thermolysis[8] and by photochemical activation.[3,4] The latter involves the use of ET photosensitizers and has been little explored.

Theoretical calculations on the ET cycloreversion of oxetane radical cations point to an initial C−C bond cleavage.[9] By contrast, the reductive ET cycloreversion should start with C−O bond breaking, according to the free energy changes calculated for the gas-phase reaction.[9] Control of the regioselectivity in the CR of oxetanes by photoinduced ET is synthetically interesting and constitutes the key step in the enzymatic repair of the (6−4) photoproducts of the DNA dipyrimidine sites by photolyase.[10−12]

Prior to our work,[13,14] only two reports have appeared on the CR of oxetane radical cations.[3,4] They have proposed that the cycloreversion of 2-aryl- and 2,2-diaryloxet-



Scheme 1



Scheme 2

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anes using cyanoaromatic compounds as ET photosensitizers proceeds with initial C2−C3 bond breaking.[3,4] The products of these reactions are the same as the reagents used to make the oxetanes. Recent experiments performed in our group have found the opposite regioselectivity in the irradiation of *trans,trans*-4-methyl-2,3-diphenyloxetane (**1a**) photosensitized by 2,4,6-triaryl(thio)pyrylium salts. The radical cation of **1a** undergoes stepwise CR with initial O−C2 bond cleavage;[14] this results in the production of *trans*-stilbene and acetaldehyde (Scheme 2, pathway b). Cleavage along pathway a is not observed. This mechanism is supported by detection of the relevant transient species (*trans*-stilbene radical cation and pyranyl radical) by means of laser flash photolysis (LFP).

Attachment of electron-releasing or -withdrawing substituents to the aryl groups could be a possible strategy to control the reaction pathway, by favouring location of the charge and the spin at different positions of the oxetane radical cation or the intermediates derived thereof. Thus, methoxy substituents are known to stabilize the positive charge of aromatic radical cations.[3,15−18] For example, in the oxidative ring opening of 2,2-diaryloxetanes,[3] the electron appears to be removed initially from an electron-rich aryl group. As a result, the strength of the C2−C3 σ bond decreases through σ−π interaction.

With this in mind, a methoxy substituent has been introduced to the 3-phenyl group of **1a**, the only oxetane known to undergo C−O cleavage upon oxidative ET photosensitized by (thio)pyrylium salts. This could lead to a reversal in regioselectivity, i.e. C2−C3 bond cleavage (Scheme 2, pathway a). In addition to product studies, LFP of **1b** could allow for the detection of either the radical cation of 4-methoxystilbene or anethole, providing direct mechanistic evidence for the ring-splitting of $\mathbf{1b}^{+\cdot}$.[19]

On the other hand, the choice of photosensitizer and the experimental conditions may determine the reaction pathways for the radical cations generated.[20] Hence, the second objective of the present work was to check whether a change of the photosensitizer could result in a reversal of the regioselectivity in the CR of **1a** and **1b**, leading to preferential cleavage along C2−C3 and O−C4 bonds (Scheme 2, pathway a).[19]

Chloranil is a well-established electron-transfer photosensitizer[21−23] that has the correct redox and spectral characteristics to enable investigation of ET processes with different excitation methods.[22] Triplet chloranil is known to react very nearly at the diffusion-controlled rate with a number of organic substrates,[21] and has been used to explore the reactivity of strained radical cations of small-ring compounds.[23] In the case of chloranil a radical ion pair is formed,[21] in contrast with (thio)pyrylium salts, where there is no net charge separation associated with the ET step.[20] Hence, the coulombic factor may be important, making the reaction more sensitive to the influence of the solvent.

Thus, the aim of the present work was to study the influence of the substitution and of the nature of the photosensitizer on the regioselectivity of the ET cycloreversion of 2,3-diaryloxetanes. As a result of this effort, clear evidence for C2−C3 bond cleavage has been obtained in the oxidative CR of oxetane **1b** using the (thio)pyrylium salts **2a** and **2b** (where *trans*-anethole radical cation is detected) and in the CR of **1a** using chloranil as alternative photosensitizer (which leads to β-methylstyrene and/or its trapping products).

Results and Discussion

Effect of Substitution on the CR Pathway

Irradiation of the oxetane **1b** was carried out in the presence of catalytic amounts of the photosensitizers **2a** and **2b**. In both cases, *trans*-anethole and benzaldehyde were detected as the sole photoproducts by direct ^{1}H NMR analysis of the reaction mixtures (Scheme 2, pathway a). These results contrast with the behaviour observed previously for the oxetane **1a**, where CR resulted in the production of *trans*-stilbene (**5a**) and acetaldehyde (Scheme 2, pathway b).

The CR reaction was found to be exergonic, starting from the triplet state of the pyrylium salts, according to the Weller equation[24] [Equation (1)], where the redox potentials (measured by cyclic voltammetry in acetonitrile) vs. SCE, were: $E_{(D+\cdot/D)}$ (**1b**) = 1.48 V,[25] $E_{(A+/A\cdot)} = -0.29$ V (**2a**) and −0.21 V (**2b**).[26]

$$\Delta G_{ET} = 23.06 \times [E_{(D+\cdot/D)} - E_{(A/A-\cdot)} + E_{coul\cdot}] - E^*_A \qquad (1)$$

The triplet energies for **2a** and **2b** are 53 and 52 kcal/mol, respectively,[27] and the coulombic factor ($E_{coul.}$) can be neglected in this case. According to simple calculations based on this equation,[24] the ET process between the ground state of **1b** and the triplet excited states of **2a** and **2b** should be thermodynamically favourable ($\Delta G_{ET} \approx -7$ and −13 kcal/mol, respectively).

As expected for a reaction involving the triplet excited state of the (thio)pyrylium salts,[25] sensitizer **2b** (with a higher intersystem crossing quantum yield)[28] was found to be more efficient than **2a**.

To elucidate the mechanism of the observed cycloreversion, LFP experiments were conducted under different conditions. In a typical experiment, LFP (355 nm) of **2b** in the presence of **1b**, using acetonitrile as solvent, gave rise to two intense signals with absorption maxima centred at ca. 380 and 600 nm, as shown in Figure 1 (A). These bands correspond to the same transient intermediate, and disappear with the same rate constant (Figure 1, B). They were ascribed to the radical cation of *trans*-anethole on the basis of literature data.[29] This assignment was confirmed by LFP of *trans*-anethole in the presence of **2b**, which gave rise to the same intermediate.

Another band peaking at 550 nm was also clearly observed in the LFP experiments performed with **2a** as photosensitizer (Figure 2, A). This band can be safely assigned to the pyranyl radical resulting from one-electron reduction of

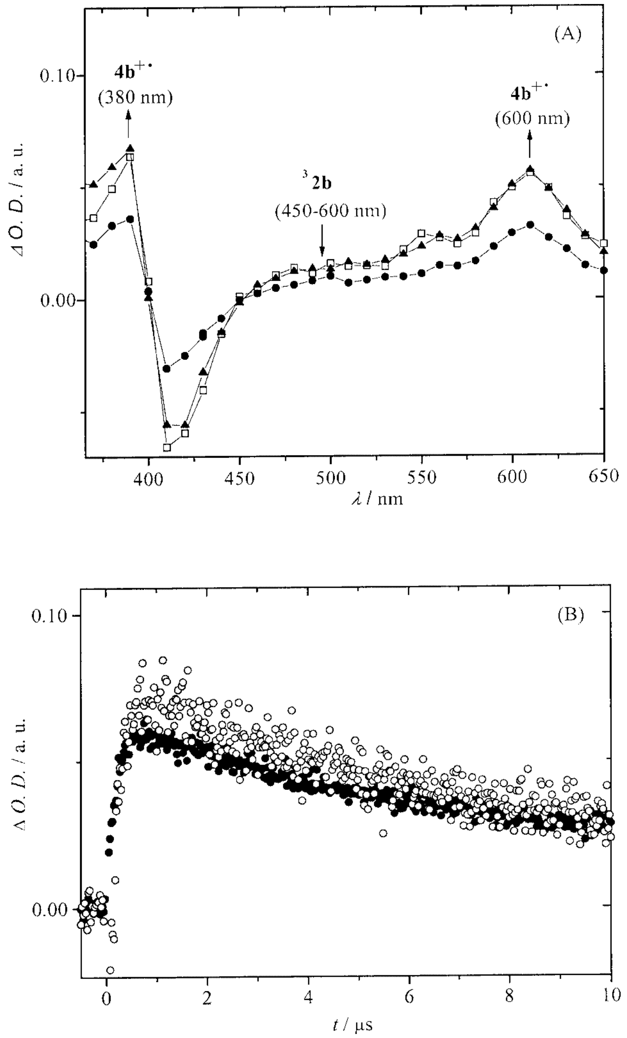


Figure 1. (A) Transient spectra obtained upon LFP (λ = 355 nm) of **2b** (0.75×10^{-4} M) in acetonitrile under argon, in the presence of **1b** (1.2×10^{-3} M); spectra recorded 0.3 µs (open squares), 1 µs (solid triangles) and 5 µs (solid circles) after the laser pulse; (B) growth and decay of the 380-nm (open circles) and 600-nm (solid circles) bands

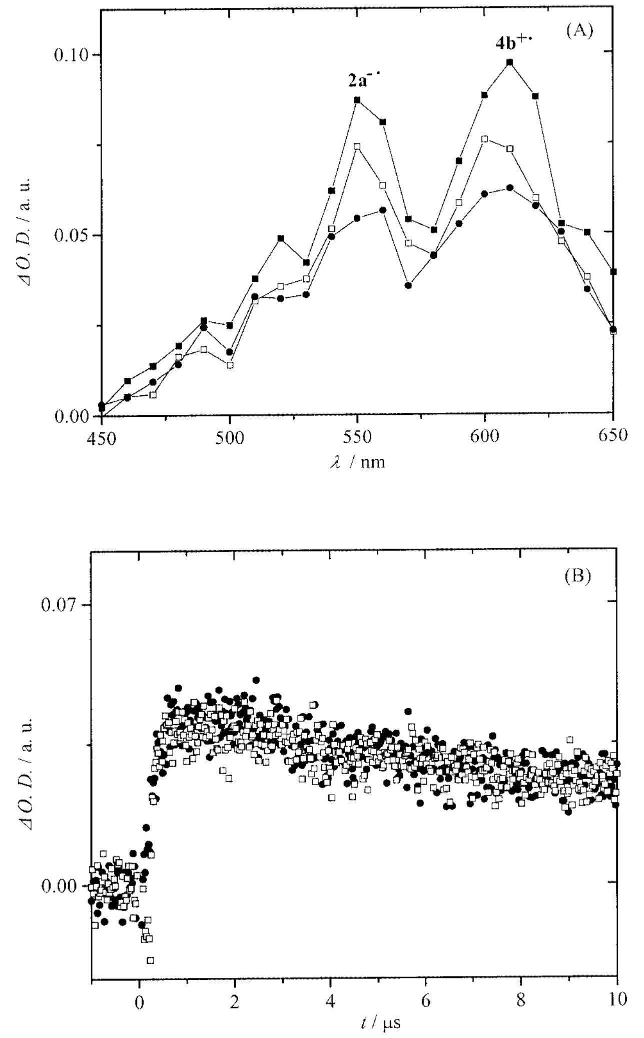


Figure 2. (A) Transient spectra obtained upon LFP (λ = 355 nm) of **2a** (1.25×10^{-4} M) in acetonitrile under argon, in the presence of **1b** (6.25×10^{-4} M); spectra recorded 1 µs (solid squares), 3 µs (open squares) and 6 µs (solid circles) after the laser pulse; (B) growth and decay of the 550-nm (open squares) and 600-nm (solid circles) bands

2a.[30] Moreover, the 4-methoxystilbene radical cation ($\lambda_{max.}$ = 500 nm)[31] was not detected; this is consistent with cleavage occurring along pathway a rather than pathway b (Scheme 2).

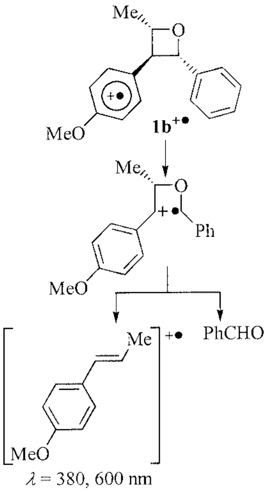
Figure 1 (B) shows the formation and decay of the 600-nm band, corresponding to the *trans*-anethole radical cation. The rate constant estimated for the initial growth is 2.5×10^{6} s^{-1}, and is independent of the concentration of **1b**. Therefore, it must be related to the splitting of the oxetane radical cation. Electron transfer from **1b** to triplet **2b** is much faster, as evidenced by the quenching rate constant (4.0×10^{9} M^{-1}s^{-1}). Hence, fragmentation of the undetectable oxetane radical cation $\mathbf{1b}^{+\cdot}$, generating the *trans*-anethole radical cation $\mathbf{4b}^{+\cdot}$ and neutral benzaldehyde, must occur in the sub-microsecond time domain. Similar results were obtained with **2a** as the photosensitizer; in this case $\mathbf{4b}^{+\cdot}$ and the pyranyl radical $\mathbf{2b}^{-\cdot}$ decayed with similar rates (Figure 2, B).

The ET behaviour of **1b** can be justified according to Scheme 3. Ionization would be likely to occur at the methoxy-substituted aromatic ring, to give $\mathbf{1b}^{+\cdot}$. Subsequent C2−C3 bond cleavage would generate a distonic 1,4-radical cation; the observed intermediate would be formed after a second (C−O) bond splitting.

The last step (formation of neutral **4b**) involves back electron transfer (BET) from $\mathbf{2}^{-\cdot}$ to $\mathbf{4b}^{+\cdot}$. Taking into account the redox potentials of **4b**, **2a** and **2b**, which are $E_{(D+\cdot/D)}$ = 1.33 V, $E_{(A/A-\cdot)}$ = −0.29 V and −0.21 V vs. SCE,[32,26] respectively, BET is highly exergonic in both cases [ΔG_{ET} ($\mathbf{4b}^{+\cdot}/\mathbf{2a}^{-\cdot}$) = −37.4 kcal/mol and ΔG_{ET} ($\mathbf{4b}^{+\cdot}/\mathbf{2b}^{-\cdot}$) = −35.5 kcal/mol].

Influence of the ET Photosensitizer on the CR Regioselectivity

Oxetane **1a** was synthesized by the Paterno−Büchi cycloaddition, according to a literature procedure.[33] Irradiation



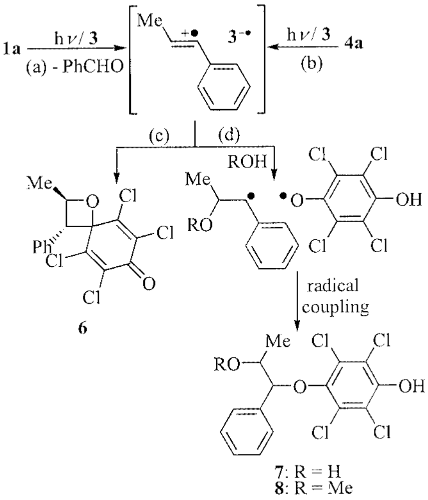
Scheme 3

Table 1. Electron transfer reactions of oxetane **1a** and alkene **4a** photosensitized by chloranil **3**

	Solvent[a]	Time [min]	Unchanged[b] **1a** or **4a**	Products[b] **5a**	**6**	**7**	**8**
1a[c]	C_6H_6	180	100	–	–	–	–
	MeCN	180	60	–	31	9	–
	MeOH	60	89	–	–	–	11
		120	77	2	–	–	21
4a[c]	C_6H_6	60	64	–	36	–	–
	MeCN	60	48	–	48	4	–
	MeOH	60	7	–	–	–	93

[a] Samples prepared in pyrex tubes; inert gas: argon, irradiation system: Luzchem multilamp photoreactor, 8 W lamps (4 ×) with emission maximum at λ = 350 nm, filter: λ > 340 nm. Samples were concentrated after irradiation and then submitted to ^{1}H NMR analysis, using $CDCl_3$ as solvent. [b] Given in %. [c] Concentration of **1a** (or **4a**) and **3**: 10^{-2} M.

of equimolar solutions of **1a** and **3** (ca. 0.01 M) was performed using benzene, acetonitrile and methanol as solvents. The results are shown in Scheme 4 and Table 1, together with those obtained for the related alkene **4a**.



Scheme 4

Whereas no photoproducts were found upon the irradiation of **1a** in benzene, formation of benzaldehyde and two new photoproducts, **6** (major) and **7** (minor) was observed in acetonitrile. *trans*-Stilbene (**5a**), acetaldehyde or stilbene−chloranil adducts were not detected in the irradiated mixture.[22] In the case of *trans*-β-methylstyrene (**4a**), the results were similar under the same experimental conditions, although shorter irradiation times were required. This was expected in view of the much higher reactivity of aryl olefins. In addition, the spirooxetane **6** was found even with benzene as the solvent. Other possible reactions of alkenes,[34] such as isomerization or dimerization, did not take place.

Formation of **6** may be explained by ring-splitting of $\mathbf{1a}^{+\cdot}$ (or ionization of **4a**) followed by reaction of the chloranil radical anion $\mathbf{3}^{-\cdot}$ with the alkene radical cation $\mathbf{4a}^{+\cdot}$ (Scheme 4, pathway c). Similar nucleophilic additions have been described previously for the irradiation of **3** in the presence of alkenes.

Formation of **7** (observed only in acetonitrile) may be explained by nucleophilic attack of residual water on the β-position of the *trans*-β-methylstyrene radical cation ($\mathbf{4a}^{+\cdot}$) and subsequent reaction of the resulting benzylic radical with the hydroquinone radical arising from protonation of the chloranil radical anion (Scheme 4, pathway d). These results are consistent with LFP observations of the chloranil radical anion ($\lambda_{max.}$ = 450 nm) and the hydroquinone radical ($\lambda_{max.}$ = 430−440 nm).[22,23a]

When methanol was used as the solvent, irradiation of equimolar solutions of **1a** and **3** led to **8** as the major photoproduct (Scheme 4, pathways a + d); after prolonged irradiation (2 h) traces of other photoproducts such as *trans*-stilbene (**5a**) and a methanol adduct[35,36] were also detected in the photomixtures. In this solvent, the spirooxetane **6** was not observed.

The formation of **8** can be explained in the same manner as that for **7** (see above), but with methanol instead of water acting as nucleophile. The same product **8** was obtained from the irradiation of **4a** in methanol using **3** as a photosensitizer (Scheme 4, pathways b + d). The different reactivities in acetonitrile and methanol can be explained taking into account the possibility of nucleophilic attack by methanol on the radical ion pair. This allows trapping of the olefin radical cation and prevents its reaction with the chloranil radical anion.

The methoxy-substituted oxetane **1b** was also irradiated in the presence of **3** in benzene and acetonitrile. In all cases, CR resulted in the formation of benzaldehyde and *trans*-anethole **4b**. *trans*-4-Methoxystilbene (**5b**), acetaldehyde or chloranil adducts were not found in the irradiation mixtures. The absence of chloranil-derived products may be due to the greater delocalization of the radical cation in the presence of the methoxy substituent. This is consistent with the fact that no product of this type was found upon irradiation of *trans*-anethole and chloranil under the same conditions.[22a]

Time-resolved studies were conducted on mixtures of **3** and **1a** in acetonitrile, benzene and/or methanol. In all cases, the decay of triplet chloranil was faster in the presence of oxetane. In a typical experiment, LFP (355 nm) of **3** in the presence of **1a**, using acetonitrile as solvent, resulted in the formation of two bands with absorption maxima at ca. 450 nm and 430 nm, corresponding to chloranil radical anion and the hydroquinone radical, respectively (Figure 3).[22,23a]

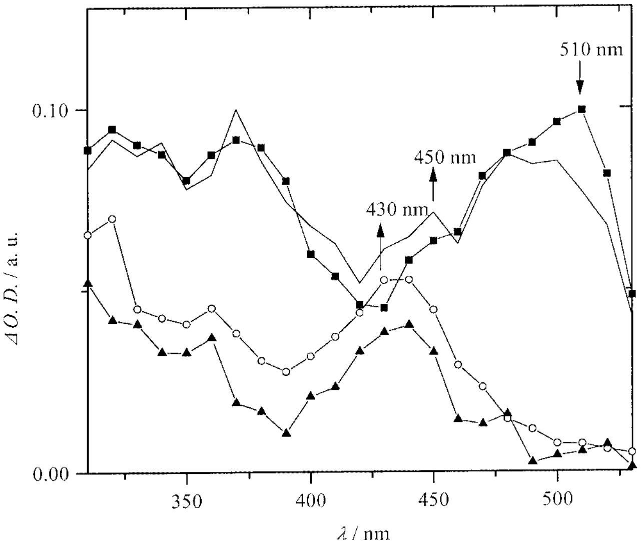


Figure 3. Transient spectra obtained upon LFP (λ = 355 nm) of **3** (5×10^{-4} M) in acetonitrile under argon, in the presence of **1a** (1.2×10^{-2} M); spectra recorded 0.4 µs (solid squares), 0.08 µs (straight line), 5 µs (open circles) and 8 µs (solid triangles) after the laser pulse

No band related to the oxetane or the arylalkene radical cations (resulting from cleavage of **1a**) was observed. This may be due to the fact that the radical cations derived from **1a** are very short-lived and cannot be detected under our reaction conditions. Actually, LFP of **3** in the presence of **4a** did not lead to any signal attributable to $\mathbf{4a}^{+\cdot}$ either. As stated above, *trans*-anethole radical cation $\mathbf{4b}^{+\cdot}$ gives rise to a typical transient absorption at ca. 600 nm and is produced during the oxidative CR of **1b** photosensitized by (thio)pyrylium salts. For this reason, oxetane **1b** was submitted to parallel studies using chloranil as ET photosensitizer. In these experiments, transient absorption spectra with two bands at 450 nm and 600 nm were clearly observed (Figure 4). They correspond to the chloranil radical anion plus the *trans*-anethole radical cation; the assignment was made on the basis of the literature data.[22,23a,29] This is consistent with the results of preparative photolysis, showing that the chloranil-photosensitized CR of **1b** proceeds with the same regioselectivity as that of **1a**, leading to *trans*-anethole.

The triplet quenching rate constants $k_q(T_1)$ were determined by LFP from the time profiles obtained for the decay of the triplet-triplet absorption of **3**, measured at 510 nm[22,23a] in the presence of increasing amounts of **1a**, **1b**, **4a** or **4b** in benzene, methanol and acetonitrile. A typical example is shown in Figure 5.

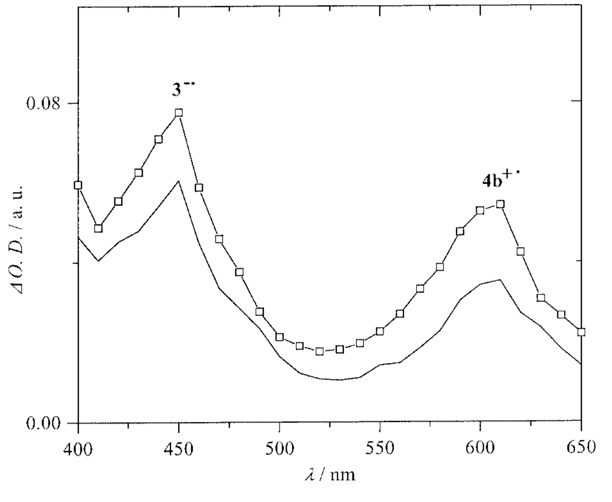


Figure 4. Transient spectra obtained upon LFP (λ = 355 nm) of **3** (5×10^{-4} M) in acetonitrile under argon, in the presence of **1b** (2.9×10^{-3} M), spectra recorded 0.3 µs (open squares) and 1 µs (line) after the laser pulse

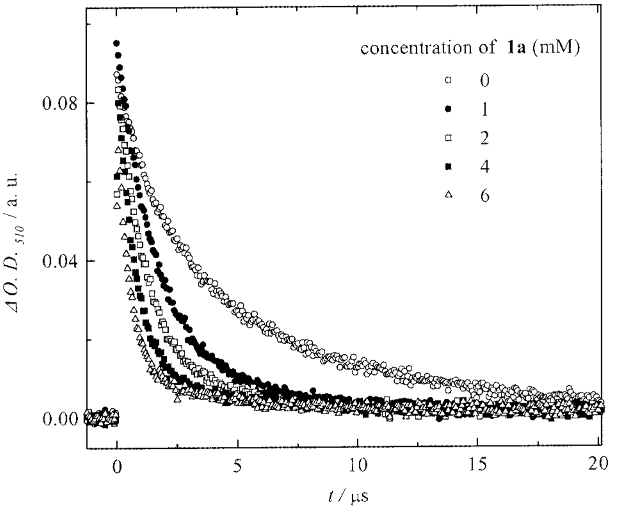


Figure 5. Decay traces of the T−T absorption of **3** (10^{-3} M) measured at 510 nm in the presence of increasing amounts of **1a**, using acetonitrile as solvent

By plotting the reciprocal lifetimes (1/τ) against the concentration of oxetane (or arylalkene), linear relationships were obtained, as shown in Figure 6.

The slopes of the straight lines correspond to $k_q(T_1)$, as deduced from Equation (2). Data are presented in Table 2, and good correlation coefficients were found in all cases.

$$1/\tau = k_o + k_q\,(T_1)\,[\text{quencher}] \qquad (2)$$

Results showed that triplet quenching in benzene is very slow compared to that found in acetonitrile and methanol, and the reaction rate of the oxetane is lower than that of the olefin. Moreover, in the presence of the methoxy substituent in the aryl group, electron transfer is faster. This is related to the free energy changes associated with electron

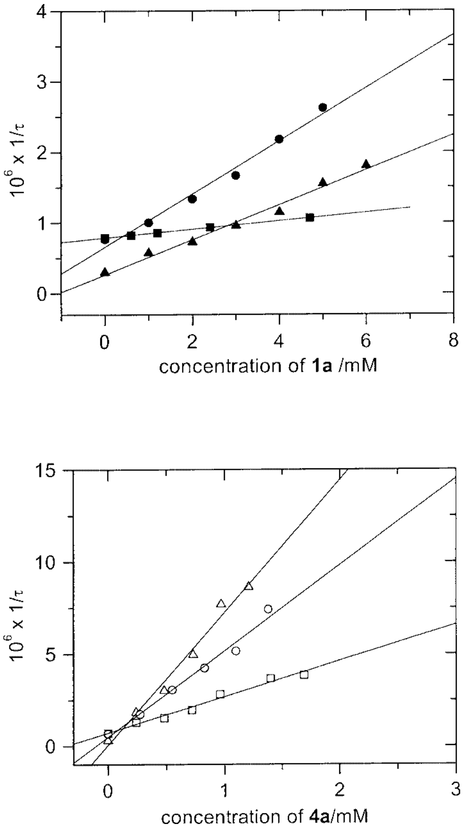


Figure 5. Plot to obtain $k_q(T_1)$ for quenching of triplet **3** by **1a** (top) and **4a** (bottom) in several solvents: C_6H_6 (squares), MeCN (triangles) and MeOH (circles)

Table 2. Thermodynamics and kinetics of the ET reaction of **1a**, **1b**, **4a** and **4b** photosensitized with the triplet excited state of **3**

	Solvent	$10^{-9} \times k_q(T_1)$[a]	$\Delta G_{ET}(T_1)$[b]
1a	C_6H_6	< 0.1	+13
	MeCN	0.3	−7
	MeOH	0.4	−7
1b	C_6H_6	0.9	+3.8
	MeCN	6.5	−16
	MeOH	3.9	−16
4a	C_6H_6	1.9	+7
	MeCN	7.2	−12
	MeOH	4.7	−13
4b	C_6H_6	3.6	+0.3
	MeCN	10.7	−19
	MeOH	9.6	−19

[a] Given in $s^{-1}M^{-1}$. [b] Given in kcal/mol.

transfer from the triplet excited state of the sensitizer, calculated using the Weller's semiempirical equation[24] [see Equation (1) above].

In this case, the redox potentials $E_{D+\cdot/D}$ of **1a**, **1b**, **4a** and **4b** have been previously reported.[25,32] For **3**, it is known[21] that $E_{A/A-\cdot} = -0.02$ V vs. SCE and $E_T = 49$ kcal/mol. The coulombic interaction is +0.79 eV in benzene, −0.06 eV in acetonitrile and −0.05 eV methanol.[37,38] The $\Delta G_{ET}(T_1)$ values were obtained taking the above data into account; the results are also given in Table 2. According to these results, the reaction should be possible in all cases, except for the oxetane **1a** in benzene. This is in agreement with the observation that no photoproduct was obtained in the irradiation of mixtures of **1a** and **3** in benzene. Thus, the coulombic factor appears to be very important in this case, in order to make the electron transfer process favourable.

Conclusion

Overall, the above results are consistent with C2−C3 bond breaking of the oxetane radical cations. This contrasts with the previous findings on the cycloreversion of the *trans,trans*-4-methyl-2,3-diphenyloxetane (**1a**) photosensitized by pyrylium salts, where initial O−C2 bond cleavage was found to occur. The reaction mechanism is supported by formation of β-methylstyrenes (or photoproducts derived thereof) and by the detection of anethole radical cations rather than 4-methoxystilbene radical cations.

In the case of pyrylium salts, the reaction would be expected to occur at the free ion stage; in contrast, the contribution of the solvent-separated ion pairs should be higher when using chloranil as the photosensitizer. Regarding this point, it is interesting to make a comparison with the splitting modes of the molecular ions in the mass spectrometer; this could be related to cleavage of the oxetane radical ions in the gas phase in the absence of a counter anion, with a high excess of energy. Indeed, the radical cations of both **4a/b** and **5a/b** are formed upon electron impact mass spectrometry of **1a** and **1b**. Finally, methoxy substitution at the 3-position of the aryl group induces C2−C3 cleavage of 2,3-diaryloxetane radical cations, which is independent of the photosensitizer employed. Thus, the regioselectivity of ET-mediated CR of oxetanes can be controlled either by modifying the substitution pattern or by changing the nature of the electron transfer photosensitizer.

Experimental Section

Chemicals: Pyrylium salt **2a**, chloranil (**3**), *trans*-β-methylstyrene (**4a**) and *trans*-anethole (**4b**) are commercially available. The thiapyrylium salt **2b** was synthesized according to the procedure described by Wizinger and Ulrich.[39] The oxetanes **1a** and **1b** were prepared by the Paterno−Büchi photocycloaddition of benzaldehyde and *trans*-β-methylstyrene[33] or *trans*-anethole,[40] according to literature procedures. Characterization was achieved by ^1H and ^{13}C NMR spectra, which were recorded with a Varian Gemini 300 spectrometer at 300 MHz and 75 MHz, respectively. Data for the known compounds was consistent with that found in the literature.

Time-Resolved Absorption Spectroscopy: The laser flash photolysis system was based on a pulsed Nd (YAG SL404G-10, Spectron Laser Systems), using 355 nm radiation as the excitation wavelength. The single pulses were of ca. 10 ns duration and the energy was ca. 20 mJ/pulse. A Lo255 Oriel xenon lamp was employed as the detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a 77200 Oriel monochromator, an Oriel photomultiplier (PMT) system (made up of a 77348 side-on PMT tube, a 70680 PMT housing and a 70705 PMT power supply). A TDS-640A Tektronix oscilloscope was used. The output signal from the oscilloscope was transferred to a personal computer for study.

Cycloreversion Procedure Using (Thio)pyrylium Salts as PET Sensitizers: The following conditions were used: oxetane **1b**: 4×10^{-2} M; **2a/b**: 2×10^{-3} M; solvent: $CDCl_3$ (0.8 mL); inert gas: argon; time: 15 min. Irradiation was performed in a photoreactor, using 4 × 8 W lamps with an emission maximum $\lambda_{max.} = 350$ nm and filter $\lambda > 340$ nm. There was no reaction in the dark or in the absence of the photosensitizer. Reactions were monitored by ^1H NMR, recorded before and after irradiation.

PET-Irradiation Procedure Using Choranil as the Electron Acceptor: Solutions of **1a** (0.01 M) and **3** (0.01 M) in the required solvent (benzene, acetonitrile and methanol) were placed in Pyrex tubes. Argon was then bubbled through the solutions for 30 min. They were irradiated in a multilamp photo reactor, using 4 × 8 W lamps with an emission maximum $\lambda_{max.} = 350$ nm and filter $\lambda > 340$ nm. There was no reaction in the dark or in the absence of the photosensitizer. After irradiation, reaction mixtures were concentrated and analyzed by ^1H NMR in deuterated chloroform. Results were compared with those obtained for the irradiation of **4a** and **3** under the same conditions. A similar procedure was applied for the irradiation of **1b** (0.007 M) and **3** (0.0032 M) in benzene and acetonitrile. Results were compared with those obtained for the irradiation of **4b** and **3** under the same conditions. Structural assignment was performed by comparison with authentic samples obtained by an alternative synthesis, namely irradiating chloranil **3** in the presence of *trans*-β-methylstyrene **4a**.

5,6,8,9-Tetrachloro-3-methyl-4-phenyl-2-oxaspiro[3,5]nona-5,8-dien-7-one (6): Solutions of *trans*-β-methylstyrene (**4a**, 0.53 g, 4 mmol) and chloranil (**3**, 0.53 g, 2 mmol) in benzene (100 mL) were placed in Pyrex tubes and irradiated for 4 h in the multilamp photo reactor ($\lambda_{max.} = 350$ nm, filter $\lambda > 340$ nm). After this time, the solution was concentrated (to 10 mL) to precipitate unchanged chloranil, which was filtered off. The filtrate containing **6** was concentrated to dryness and the resulting dark orange solid was repeatedly recrystallized from benzene/petroleum ether, until a white solid **6** (30 mg, 4.1%) was obtained. ^1H NMR (300 MHz, TMS as internal standard, $CDCl_3$, 25 °C): $\delta = 1.78$ (d, $J = 6.2$ Hz, 3 H, CH_3), 4.60 (d, $J = 8.3$ Hz, 1 H, 4-H), 5.80 (m, 1 H, 3-H), 6.89 (m, 2 H, CH, phenyl), 7.29 (m, 3 H, CH, phenyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 21.8$ (CH_3), 57.3 (CH), 79.0 (CH), 86.8 (C), 125. 9 (CH), 128.1 (CH), 128.8 (CH), 130.5 (C), 131.7 (C), 133.7 (C), 151.4 (C), 152.0 (C), 169.7 (C) ppm. $C_{15}H_{10}Cl_4O_2$ (364.044): calcd. C 49.50, H 2.75, Cl 38.96; found C 49.00, H 2.66, Cl 38.71.

2,3,5,6-Tetrachloro-4-(2′-hydroxy-1′-phenylpropoxy)phenol (7): Solutions of **4a** (0.35 g, 3 mmol) and **3** (0.62 g, 2.5 mmol) in acetonitrile (120 mL) were placed in Pyrex tubes and irradiated in the multilamp photo reactor for 4 h. The volume was concentrated (to 10 mL) to precipitate unchanged chloranil, which was filtered off. The filtrate was concentrated to dryness to give a dark orange precipitate, containing a mixture of **6** and **7**. The photoproduct **7** was isolated from the first crop in the recrystallization of the mixture from hot benzene/petroleum ether. It was purified by repeated recrystallization, to give **7** (12 mg, 1.3%) as a white solid. ^1H NMR (300 MHz, TMS as internal standard, $CDCl_3$, 25 °C): $\delta = 1.03$ (d, $J = 6.4$ Hz, 3 H, CH_3), 3.00 (s, 1 H, OH), 4.50 (dq, $J_1 = 6.4$, $J_2 = 7.6$ Hz, 1 H, 2′-H), 5.29 (d, $J = 7.6$ Hz, 1 H, 1′-H), 5.91 (s, 1 H, OH), 7.26−7.31 (m, 5 H, CH, phenyl) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3, 25 °C): $\delta = 19.7$ (CH_3), 70.9 (CH), 91.1 (CH), 120.7 (C), 127.5 (CH), 128.8 (CH), 129.3 (CH), 138.8 (C), 146.2 (C), 147.7 (C) ppm. $C_{15}H_{12}Cl_4O_2$ (366.0598): calcd. C 47.16, H 3.17, Cl 37.12; found C 46.56, H 2.96, Cl 36.98.

2,3,5,6-Tetrachloro-4-(2′-methoxy-1′-phenylpropoxy)phenol (8): Solutions of **4a** (0.43 g, 3.6 mmol) and **3** (0.30 g, 1.2 mmol) in methanol were placed in Pyrex tubes and irradiated in the multilamp photo reactor ($\lambda_{max.} = 350$ nm, filter $\lambda > 340$ nm) for 3 h. After this time, the solutions were partially concentrated to precipitate unchanged chloranil, which was filtered off. Subsequent concentration to dryness gave a dark orange precipitate containing **7**, which was purified by recrystallization from benzene/petroleum ether and then from benzene, until **8** (25 mg, 5.3%) was obtained as a white solid. ^1H NMR (300 MHz, TMS as internal standard, $CDCl_3$, 25 °C): $\delta = 0.90$ (d, $J = 6.3$ Hz, 3 H, CH_3), 3.36 (s, 3 H, OCH_3), 3.97 (dq, $J_1 = 6.3$, $J_2 = 7.4$ Hz, 1 H, 2′-H), 5.35 (d, $J = 7.4$ Hz, 1 H, 1′-H), 5.95 (s, 1 H, OH), 7.32−7.50 (m, 5 H, CH, phenyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 15.4$ (CH_3), 56.9 (CH_3), 80.2 (CH), 88.4 (CH), 118.7 (C), 126.6 (CH), 128.0 (CH), 128.2 (CH), 136.9 (C), 145.1 (C), 146.5 (C) ppm. $C_{16}H_{14}Cl_4O_3$ (396.0806): calcd. C 48.52, H 3.56; found C 48.44, H 3.56.

Supporting Information: Copies of the ^1H and ^{13}C NMR spectra for the new photoproducts **6**, **7** and **8** (Figures S.I.1, 2 and 3, respectively). Representative structural data used for the tentative assignment of 3-hydroxy-1-methoxy-1,2-diphenylbutane, formed in small amounts. Laser flash photolysis spectra of *trans*-anethole (**4b**) and (thio)pyrylium salts **2a**,**b** (Figures S.I.4 and 5).

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[35] A methanol adduct (tentatively assigned as 3-hydroxy-1-methoxy-1,2-diphenylbutane) was obtained in small amounts as a mixture of diastereoisomers, resulting from the nucleophilic attack of methanol on the oxetane-derived 1,4-radical cation. The structural assignment was done by comparison of the spectroscopic data (^{1}H and ^{13}C NMR, see Supporting Information) with those of related compounds.[36] The relative positions of the methoxy and hydroxy groups was confirmed by GC-MS (presence of a peak at $m/z = 121$, corresponding to $[\mathrm{PhCHOCH_3}]^+$) and by the changes in the ^{1}H NMR spectrum upon acetylation with acetyl chloride.

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[38] The coulombic interaction in a given solvent ($\Delta E_{\mathrm{coul.}}$) is derived from the Born equation as shown by Weller. Both the Coulombic attraction and the solvation entalpy were taken into account: $\Delta E_{\mathrm{coul.}}$ [eV] $= (e/4\pi\varepsilon_o a)\cdot(1/\varepsilon - 2/37.5)$, where $e = 1.602 \times 10^{-19}$ C, $\varepsilon_o = 8.854 \times 10^{-12}$ CV^{-1}m^{-1} and $a = 7$ Å. The value of ε is known to be 2.28 in benzene, 37.5 in acetonitrile and 32.7 in methanol.

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