ORGANIC
LETTERS

2001
Vol. 3, No. 13
1965−1967

Steady-State and Time-Resolved Studies on Oxetane Cycloreversion Using (Thia)pyrylium Salts as Electron-Transfer Photosensitizers

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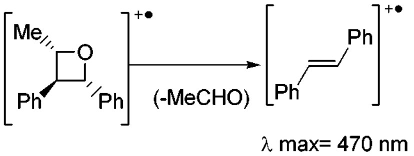
Received March 15, 2001

ABSTRACT



Cycloreversion of oxetane 1 is achieved using (thia)pyrylium salts as 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.

Cycloreversion (CR) of oxetanes by photoinduced electron transfer (PET) has recently attracted considerable interest, as this process appears to be involved in the photoenzymatic repair of the (6-4) photoproducts of the DNA dipyrimidine sites by photolyase.[1] Both radical anions and radical cations of oxetanes undergo fragmentation, though reaction with the former is more exothermic.[2]

In a preliminary study using 2,2-diaryloxetanes and cyanoaromatic compounds as electron-transfer photosensitizers, the CR reaction was found to occur through the excited singlet state of the photosensitizer.[3] Although the process was explained via formation of radical cations, no intermediate of this type was detected. In addition, cycloreversion occurred 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 was found to operate when electron-donating substituents are attached to the aryl groups.[3]

Pyrylium salts are a potentially useful group of photosensitizers.[4] They are good oxidizing agents and can be selectively excited because of their absorption in the visible.[5] On the other hand, depending on the substitution pattern and the reaction conditions, they can generate radical ion pairs of different multiplicity (singlet or triplet).[6,7] Thus it 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. In the present work, we have chosen the diphenyl-substituted oxetane **1**[8] and a series of pyrylium and thiapyrylium salts **2a−d** as model compounds

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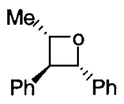
10.1021/ol0158516 CCC: $20.00

to study the photosensitized electron-transfer cycloreversion of oxetanes and to gain further insight into the mechanistic aspects of this reaction.



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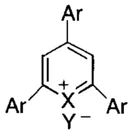

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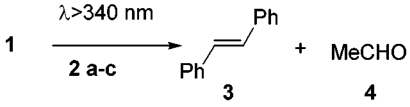
sensitizer	X	Y	Ar
2a	O	BF_4	Ph
2b	S	ClO_4	Ph
2c	O	BF_4	p-Br-C_6H_4
2d	O	BF_4	p-MeO-C_6H_4

When oxetane **1** was irradiated (λ > 340 nm) using catalytic amounts of pyrylium salts **2a**−**d**, CR was observed, resulting in the production of *trans*-stilbene and acetaldehyde as the only photoproducts (Scheme 1).

Scheme 1



The reaction yields are given in Table 1. Control experiments showed that no photocycloreversion takes place in the dark or in the absence of the photosensitizer. Further control experiments (data not given in Table 1) clearly showed that neither the photosensitizer concentration (up to 10^{-2} M) nor the nature of the counteranion (BF_4^- or ClO_4^-) produced significant effects on the obtained results.

Table 1. Cycloreversion of Oxetane **1** Photosensitized by Pyrylium Salts **2a**−**d**

sensitizer	CR (%)[a]	CR (ϕ)[b,c]
2a	8[d]	0.02
2b	100	0.10
2c	33[d]	0.04
2d		

[a] Oxetane **1**, 4.7 × 10^{-2} M; sensitizer, 10^{-3} M; solvent, $CDCl_3$; filter, λ > 340 nm; Luzchem multilamp photoreactor, 8 W lamps (4×) with emission maximum at 300 nm. [b] Oxetane **1**, 10^{-4} M; sensitizer, 2.5 × 10^{-5} M; solvent, CH_3CN; lamp, Xenon 450 W, monochromatic light of λ = 420 nm; actinometer, potassium ferrioxalate. The solutions were placed in sealed cuvettes and bubbled with argon for 15 min to achieve deoxygenation.[c] No significant CR reaction was observed in the presence of oxygen. [d] The rest was unreacted starting material.

To obtain more reliable quantitative data, the CR quantum yield was measured using potassium ferrioxalate as actinometer.[9] The results are also given in Table 1. These results clearly show that (a) the CR is photosensitized by pyrylium salts, (b) it produces carbonyl and olefin units different from the reagents employed in the Paterno−Büchi process, and (c) the most efficient photosensitizer is the thiapyrylium salt **2b**. Moreover, the fact that the quantum yields were much less than unity suggest that a chain reaction is not involved.

To elucidate the reaction mechanism actually operating, a laser flash photolysis (LFP) study was performed. In a typical experiment, LFP (355 nm) of a mixture of **1** and **2b** in CH_3CN gave a transient with an absorption maximum at 470 nm (Figure 1), which can be ascribed to the radical cation of *trans*-stilbene on the basis of literature data.[7,10]

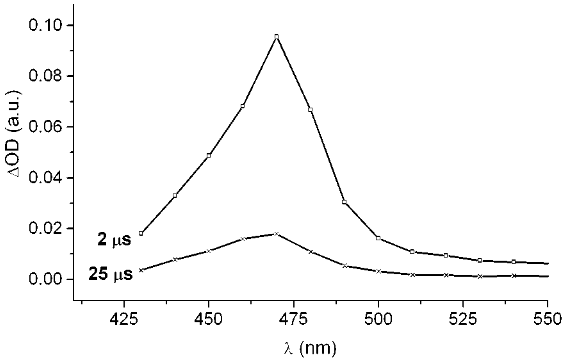


Figure 1. Transient spectra obtained from LFP (λ = 355 nm) of **1** (1.2 × 10^{-4} M) and **2b** (10^{-4} M) in acetonitrile, under argon.

This confirmed that photocycloreversion of oxetane **1** follows an electron-transfer mechanism and indicated that splitting of the four-membered ring gives rise to the radical cation of *trans*-stilbene instead of the radical cation of 1-phenylpropene. In principle the PET process between **1** and **2** might involve either the excited singlet or triplet of the pyrylium salt. To check the feasibility of the two pathways, the free energy change associated with electron transfer was calculated using the Weller[11] equation (eq 1) for both excited states.

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

The $E_{D^{+\bullet}/D}$ for **1** was measured by cyclic voltammetry in acetonitrile and found to be 1.42 V vs SCE. On the other hand, the singlet and triplet energies of the sensitizers had been previously measured.[4] Using these values, the PET reaction was found to be exothermic in all cases (Table 2).

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Table 2. Thermodynamics of the PET Reaction between **1** and **2a**−**d**

sensitizer	$E_{(\mathrm{A/A^{-\bullet}})}$ [a]	E(S) [b,c]	E(T) [b,c]	ΔG(S) [b]	ΔG(T) [b]
2a	2.53	66	53	−24	−11
2b	2.59	66	52	−26	−12
2c	2.49	63	na [d]	−23	na [d]
2d	1.98	58	51	−11	−4

[a] Given in V (vs SCE). [b] Given in kcal/mol. [c] Taken from the literature.[4] [d] na: not available.

To gain further insight into the reaction mechanism, quenching of the pyrylium salts fluorescence by the oxetane was investigated. Pyrylium salt concentration was fixed by adjusting the absorbance of the solutions at the arbitrary value of 0.19. Then, the fluorescence intensities (I) observed upon addition of different concentrations of **1** ([Q]) were used to calculate the Stern−Volmer constants (K). A linear fit was observed in all cases according to the equation $I_0/I = 1 + K[Q]$. These values together with the fluorescence lifetimes (measured by time-resolved emission spectroscopy) were used to calculate the quenching rate constants (k_q). The results are shown in Table 3. From these data it is clear that fluorescence quenching occurs at a nearly difusion-controlled rate, except in the case of the methoxy derivative **2d** (Table 3).

Table 3. Deactivation (Fluorescence and Intersystem Crossing) of the Excited Singlet of **2a**−**d**

sensitizer	$10^{-8} \times k_f$ [a,b]	$10^{-8} \times k_{isc}$ [a,b]	ϕ_{isc} [b]	$10^{-9} \times k_q$ [c]
2a	1.1	1.2	0.53	6.8
2b	0.1	2.1	0.94	6.9
2c	2.5	5.1	0.67	10.6
2d	1.8	<0.1	0.03	

[a] Given in s^{-1} and taken from the literature.[4] [b] In the absence of quencher. [c] Fluorescence quenching by oxetane **1**, given in s^{-1} M^{-1}.

Thus, the cycloreversion reaction might in principle occur from both excited states; however, the fact that the pyrylium salt **2b**, with the highest intersystem crossing quantum yield, is the most efficient sensitizer points clearly to triplet involvement (Scheme 2).

This is also supported by the fact that the reaction does not occur in the presence of oxygen, a good triplet quencher. To make sure that the triplets of **2a**−**c** are formed in sufficient amount, even at high oxetane concentrations, it appeared necessary to calculate the relative contributions of the different singlet deactivation pathways under the employed reaction conditions (Table 4).

Scheme 2

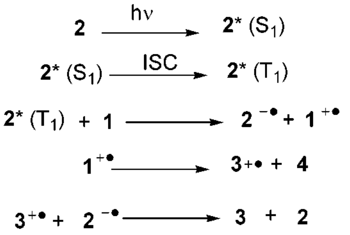

Table 4. Relative Contribution of the Different Pathways Resulting in Deactivation of the Excited Singlet of **2a**−**d** at Two Concentrations of **1**

[**1**] (M)	sensitizer	Q (%) [a]	F (%) [b]	ISC (%) [c]
10^{-2}	**2a**	23	36	41
	2b	23	5	72
	2c	12	29	59
	2d		97	3
10^{-4}	**2a**	11	46	53
	2b	1	6	93
	2c	1	33	66
	2d		97	3

[a] Singlet quenching. [b] Fluorescence. [c] Intersystem crossing.

It is interesting that thiapyrylium salt **2b** produces the highest amount of triplets at the two oxetane concentrations, followed by the tribromo derivative **2c** and the parent compound **2a**. This correlates well with the relative CR efficiencies given in Table 1. In the case of the trimethoxy analogue **2d**, the almost exclusive deactivation pathway is fluorescence; neither singlet quenching nor intersystem crossing occur to a significant extent.

In summary, the electron-transfer cycloreversion of the model oxetane**1** can be achieved by photosensitization with triaryl(thia)pyrylium salts. The reaction takes place from the excited triplet state of the photosensitizers and ensues with splitting of **1** into acetaldehyde plus the *trans*-stilbene radical cation, which can be detected by 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 DGES (Grant PB 97-0339 and FP98) is gratefully acknowledged.

OL0158516