

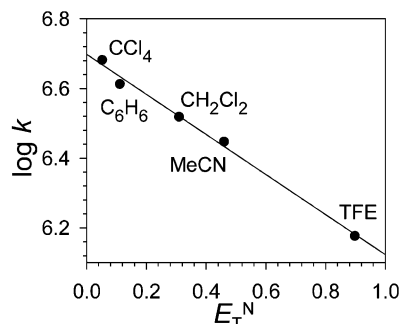
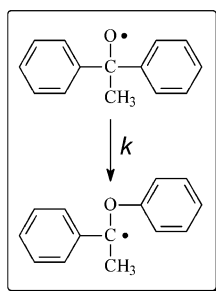
Solvent Effects on the *O*-Neophyl Rearrangement of 1,1-Diarylalkoxy Radicals. A Laser Flash Photolysis Study

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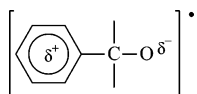
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A laser flash photolysis study has been carried out to assess solvent effects on the *O*-neophyl rearrangement of 1,1-diarylalkoxy radicals. The rearrangement rate constant k decreases by increasing solvent polarity and an excellent correlation with negative slope is obtained between $\log k$ and the solvent polarity parameter E_T^N . These evidences are in full agreement with the previous indication that the extent of internal charge separation decreases on going from the starting 1,1-diarylalkoxy radical to the transition state.

We have recently provided evidence that the *O*-neophyl rearrangement of 1,1-diarylalkoxy radicals proceeds through a concerted mechanism (Scheme 1, path **a**) and not, as previously suggested,^{2,3} through a stepwise mechanism via formation of a bridged 1-oxaspiro[2.5]octadienyl radical intermediate (Scheme 1, paths **b** and **c**).

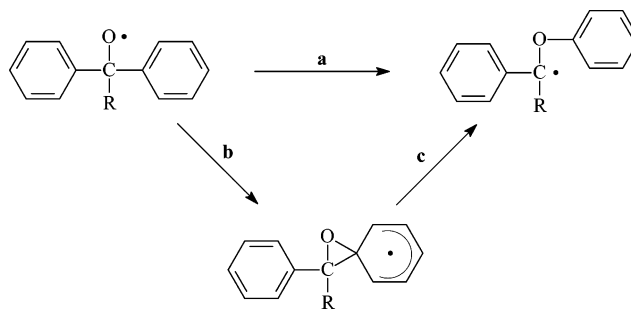
In this study it was proposed that the rearrangement transition state is characterized by a limited extent of carbon radical character.¹ Moreover, following the indication of the existence of a certain degree of internal charge transfer in arylcarbinoyl radicals, with the oxygen atom bearing a partial negative charge and the partial positive charge delocalized over the aromatic ring,⁴ it was



also suggested that the extent of charge separation

- (1) Aureliano Antunes, C. S.; Bietti, M.; Ercolani, G.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 3884–3891.
- (2) Grossi, L.; Strazzari, S. *J. Org. Chem.* **2000**, *65*, 2748–2754.
- (3) Banks, J. T.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 3527–3531.
- (4) Avila, D. V.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576–6577.

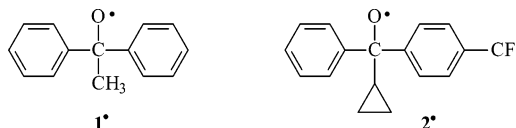
SCHEME 1



decreases on going from the initial 1,1-diarylalkoxy radical to the transition state.¹ These observations were rationalized in terms of a reactant-like transition state.

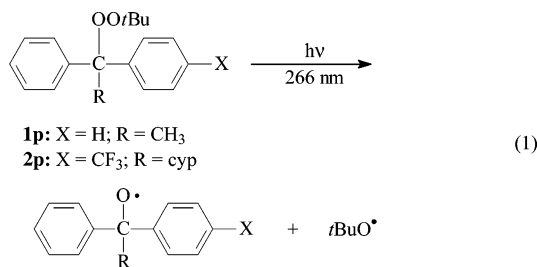
In particular, the indication of a decrease in the extent of charge separation clearly suggests that solvent effects should play a role on the *O*-neophyl rearrangement of 1,1-diarylalkoxy radicals.

Solvent effects on alkoxy radical reactivity have been studied in detail for hydrogen atom abstraction,^{5–12} β -scission,^{11–18} and 1,2-hydrogen atom shift¹⁹ reactions; no information in this respect is instead available for the *O*-neophyl rearrangement. Along this line, and in order to gain additional support to the mechanistic picture presented above, we have carried out a laser flash photolysis study on the reactivity of the 1,1-diphenylethoxy radical **1**[•] in different solvents. As a matter of comparison, some experiments have been also carried out for the α -phenyl- α -(4-trifluoromethylphenyl)cyclopropylmethoxy radical **2**[•].



- (5) Aliaga, C.; Stuart, D. R.; Aspée, A.; Scaiano, J. C. *Org. Lett.* **2005**, *7*, 3665–3668.
- (6) Snelgrove, D. W.; Luszyk, J.; Banks, J. T.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469–477.
- (7) de Heer, M. I.; Mulder, P.; Korth, H.-G.; Ingold, K. U.; Luszyk, J. *J. Am. Chem. Soc.* **2000**, *122*, 2355–2360.
- (8) MacFaul, P. A.; Ingold, K. U.; Luszyk, J. *J. Org. Chem.* **1996**, *61*, 1316–1321.
- (9) Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Luszyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966–9971.
- (10) Avila, D. V.; Ingold, K. U.; Luszyk, J.; Green, W. H.; Procopio, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 2929–2930.
- (11) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Luszyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466–470.
- (12) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69–80 and references therein.
- (13) Bietti, M.; Gente, G.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 6820–6826.
- (14) Newcomb, M.; Daublain, P.; Horner, J. H. *J. Org. Chem.* **2002**, *67*, 8669–8671.
- (15) Baciocchi, E.; Bietti, M.; Salamone, M.; Steenken, S. *J. Org. Chem.* **2002**, *67*, 2266–2270.
- (16) Weber, M.; Fischer, H. *J. Am. Chem. Soc.* **1999**, *121*, 7381–7388.
- (17) Tsentlovich, Y. P.; Kulik, L. V.; Gritsan, N. P.; Yurkovskaya, A. V. *J. Phys. Chem. A* **1998**, *102*, 7975–7980.
- (18) Bacha, J. D.; Kochi, J. K. *J. Org. Chem.* **1965**, *30*, 3272–3278.
- (19) Konya, K. G.; Paul, T.; Lin, S.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **2000**, *122*, 7518–7527.

Radicals **1**[•] and **2**[•] have been generated in MeCN, MeCN/H₂O 1:1, CF₃CH₂OH (TFE), and CH₂Cl₂ by 266 nm laser flash photolysis (LFP) of the parent *tert*-butyl peroxides **1p** and **2p** (method 1) as described in eq 1:

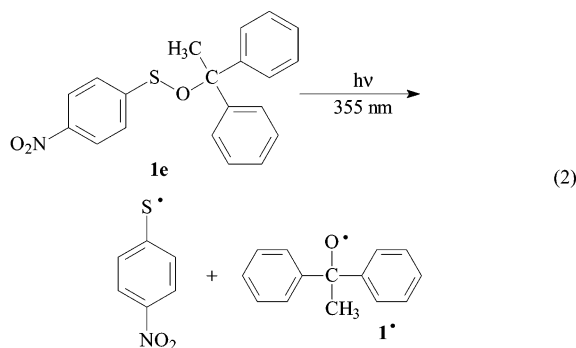


The spectral properties and reactivities of radicals **1**[•] and **2**[•] in MeCN have been described previously.¹ Both radicals display a broad absorption band in the visible region of the spectrum, centered at 530 and 520 nm, respectively, which is unaffected by oxygen. This band was observed to undergo a first-order decay, leading in both cases to a corresponding strong increase in absorption in the UV region of the spectrum, assigned to the rearranged carbon centered radical formed by aryl shift in the 1,1-diaryloxy radical (Scheme 1).

As compared to MeCN, in MeCN/H₂O 1:1 and TFE a red shift in the position of the visible absorption band maximum of 10–20 nm was observed for both radicals, in line with that observed previously for related aryl-carbinyloxy radicals.^{13,15}

The decay of radicals **1**[•] and **2**[•] generated by method 1 in MeCN, MeCN/H₂O 1:1, TFE, and CH₂Cl₂ was measured spectrophotometrically by monitoring the decrease in optical density at the corresponding visible absorption maxima and was found to follow first-order kinetics. The corresponding rearrangement rate constants thus obtained are reported in Table 1 together with the visible absorption band maximum wavelengths.

However, because method 1 could not be employed for alkoxy radical generation in solvents such as benzene and CCl₄, radical **1**[•] was also generated in MeCN, benzene, and CCl₄ by 355 nm LFP of the parent 4-nitrobenzenesulfonate ester **1e** (method 2) as described in eq 2.^{14,20}



The time-resolved absorption spectra observed after 355 nm LFP of an argon-saturated MeCN solution containing 4-nitrobenzenesulfonate ester **1e** are dis-

TABLE 1. Visible Absorption Band Maximum Wavelengths and Decay Rate Constants for 1,1-Diaryloxy Radicals **1**[•] and **2**[•] Measured in Different Solvents at *T* = 22 °C under Argon

radical	solvent	method of generation ^a	λ_{\max} (vis)/nm ^b	k_t/s^{-1c}
1 [•]	MeCN	1	530	2.8×10^6 ^d
	MeCN	2	<i>e</i>	2.9×10^6 ^f
	MeCN	2	<i>e</i>	2.9×10^6 ^{f,g}
	MeCN/H ₂ O ^h	1	540	2.3×10^6
	TFE	1	540	1.5×10^6
	CH ₂ Cl ₂	1	530	3.3×10^6
	benzene	2	<i>e</i>	4.1×10^6 ^f
2 [•]	CCl ₄	2	<i>e</i>	4.8×10^6 ^f
	MeCN	1	520	5.0×10^6 ^d
	MeCN/H ₂ O ^h	1	540	4.5×10^6
	TFE	1	540	2.2×10^6
CH ₂ Cl ₂	1	520	7.3×10^6	

^a Method 1: 266 nm LFP of peroxides **1p** and **2p** (eq 1). Method 2: 355 nm LFP of 4-nitrobenzenesulfonate ester **1e** (eq 2). ^b Visible absorption band maximum of the 1,1-diaryloxy radical. ^c Measured following the decay of the 1,1-diaryloxy radical at the visible absorption band maximum. ^d Reference 1. ^e Under these conditions, the superimposition of the 4-nitrobenzenethiyl radical (4-NBS[•]) and 1,1-diphenylethoxy radical (**1**[•]) absorption bands (see text) did not allow the determination of λ_{\max} (vis). ^f Measured following the fast component of the double exponential decay in the 440–570 nm range. ^g Oxygen saturated. ^h MeCN/H₂O 1:1 (v/v).

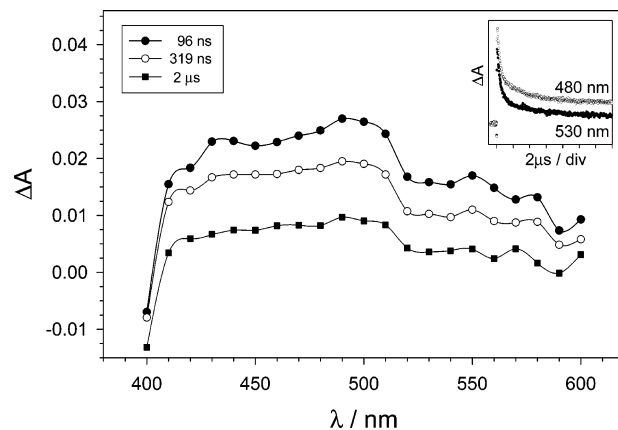


FIGURE 1. Time-resolved absorption spectra observed after 355 nm LFP of **1e** (8.0×10^{-5} M) in an argon-saturated MeCN solution at 96 ns (●), 319 ns (○), and 2 μ s (■) after the 8 ns, 10 mJ laser pulse. Inset: decay of absorption monitored at 480 nm (○) and 530 nm (●).

played in Figure 1. The spectrum recorded after 96 ns is characterized by a broad absorption band between 410 and 600 nm, which on the basis of the comparison with literature data can be reasonably assigned to the superimposition of the 4-nitrobenzenethiyl radical (4-NBS[•]: $\lambda_{\max} = 480$ nm)^{14,21} and 1,1-diphenylethoxy radical (**1**[•]: $\lambda_{\max} = 530$ nm)^{1,3,22} absorption bands. This assignment is also supported by the observation that the spectrum is not influenced by oxygen, in agreement with literature data.^{1,3,21,22}

The spectrum was observed to undergo a double exponential decay in the 440–570 nm range (see, for

(21) Alam, M. M.; Ito, O. *J. Org. Chem.* **1999**, *64*, 1285–1290.

(22) Avila, D. V.; Ingold, K. U.; Di Nardo, A. A.; Zerbetto, F.; Zgierski, M. Z.; Luszytk, J. *J. Am. Chem. Soc.* **1995**, *117*, 2711–2718.

(20) Horner, J. H.; Choi, S.-Y.; Newcomb, M. *Org. Lett.* **2000**, *2*, 3369–3372.

example, the inset in Figure 1). From the double exponential fit, the decay of the two components was measured as 2.9×10^6 and $3 \times 10^5 \text{ s}^{-1}$, respectively. The former value is very similar to the rate constant measured for the rearrangement of 1^\bullet , generated by method 1 in MeCN (between 2.5 and $3.2 \times 10^6 \text{ s}^{-1}$).^{1,3,22,23} On the basis of this observation, the fast component of the double exponential decay observed in the 440–570 nm range can be reasonably assigned to the same process, i.e., the *O*-neophyl rearrangement of 1^\bullet . The slow component is instead assigned to the decay of 4-NBS.²¹

An analogous behavior was observed after 355 nm LFP of $1e$ in benzene and CCl_4 , and also in these solvents the rearrangement rate constants of 1^\bullet were determined from the first-order fit to the fast component of the double exponential decay observed in the 440–570 nm range. The rearrangement rate constants thus obtained for 1^\bullet , generated by method 2 in MeCN, benzene, and CCl_4 , are also reported in Table 1.

The kinetic data collected in Table 1 clearly show that for both 1^\bullet and 2^\bullet the rearrangement rate constant decreases by increasing solvent polarity. As an example, with 1^\bullet the rate constant decreases from 4.8×10^6 to $1.5 \times 10^6 \text{ s}^{-1}$ on going from CCl_4 to TFE. This behavior is in full agreement with the mechanistic picture presented above indicating that the *O*-neophyl rearrangement of 1,1-diaryloxy radicals involves a decrease in the extent of internal charge separation on going from the starting 1,1-diaryloxy radical to the transition state. However, because a decrease in the extent of charge separation can be expected for both the concerted and the stepwise mechanisms described in Scheme 1 (path **a** and paths **b-c**, respectively),¹ the kinetic solvent effect data displayed in Table 1 do not provide any new information that may contribute to distinguish between these two mechanistic possibilities.²⁴

Quite interestingly, an excellent correlation is obtained between the logarithm of the experimental rate constants measured for the rearrangement of the 1,1-diphenylethoxy radical 1^\bullet ($\log(k/\text{s}^{-1})$) and the normalized Dimroth-Reichardt solvent polarity parameter E_T^N (Figure 2).²⁵

An analogous correlation ($\log k_\beta$ vs E_T^N) has been reported for the β -scission reaction of the cumyloxy radical,^{11,13} where however, in contrast with the present study, the fragmentation rate constant was observed to increase by increasing solvent polarity. This behavior has

(23) Falvey, D. E.; Khambatta, B. S.; Schuster, G. B. *J. Phys. Chem.* **1990**, *94*, 1056–1059.

(24) As described previously (see ref 1), in a concerted mechanism a reactant-like transition state that is close in structure to the 1,1-diaryloxy radical can be expected. On the other hand, in a stepwise mechanism the transition state of the rate-determining step will be close in structure to the 1-oxaspiro[2,5]octadienyl radical intermediate. As compared to the latter mechanism, with the former one a significantly smaller decrease in the extent of internal charge separation on going from the starting 1,1-diaryloxy radical to the transition state should be expected. Accordingly, the observation of relatively small kinetic solvent effects in the rearrangement of 1^\bullet , with k decreasing from 4.8×10^6 to $1.5 \times 10^6 \text{ s}^{-1}$ on going from CCl_4 to TFE, may be more in line with the operation of a concerted mechanism. As a matter of comparison, significantly larger kinetic solvent effects have been observed for the β -scission reaction of the cumyloxy radical, with k increasing from 2.6×10^5 to $6.1 \times 10^6 \text{ s}^{-1}$ on going from CCl_4 to TFE (see refs 11 and 13), indicative of a relatively larger increase in the extent of charge separation on going from the cumyloxy radical to the carbonyl-like transition state.

(25) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, 2003.

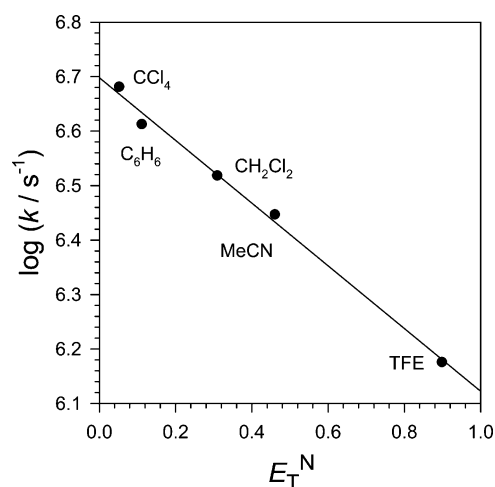


FIGURE 2. Plot of $\log(k/\text{s}^{-1})$ for the rearrangement of radical 1^\bullet against the normalized Dimroth-Reichardt solvent polarity parameter E_T^N in different solvents. From the linear regression: slope = -0.58 , $r^2 = 0.9944$.

been interpreted in terms of the stabilization of the transition state for cumyloxy radical C-Me β -scission through increased solvation of the incipient carbonyl product. As it has been pointed out that the E_T^N parameter is mainly related to the solvent anion solvating ability,²⁶ the observation of a $\log k_\beta$ vs E_T^N correlation has been explained in terms of the development of negative charge on the oxygen atom of the forming carbonyl compound. Along this line, the negative slope of the $\log k$ vs E_T^N correlation (Figure 2) observed in the *O*-neophyl rearrangement of the 1,1-diphenylethoxy radical 1^\bullet reasonably reflects the decrease in the extent of negative charge on the oxygen atom on going from the starting radical to the transition state.

In conclusion, laser flash photolysis experiments carried out in different solvents have shown that the rate constant for *O*-neophyl rearrangement of 1,1-diaryloxy radicals decreases by increasing solvent polarity. This observation provides support for the previous hypothesis that the *O*-neophyl rearrangement of 1,1-diaryloxy radicals involves a decrease in the extent of internal charge separation on going from the starting radical to the transition state. On the other hand, the kinetic solvent effect data do not provide any new information that may contribute to distinguishing between the two possible mechanisms described for the *O*-neophyl rearrangement of 1,1-diaryloxy radicals: the concerted mechanism and the stepwise one that proceeds through the formation of a bridged 1-oxaspiro[2,5]octadienyl radical intermediate.

Experimental Section

Materials. Spectroscopic grade MeCN, CH_2Cl_2 , CCl_4 , TFE, and benzene were used as received. The synthesis of peroxides **1p** and **2p** has been described previously.¹ 4-Nitrobenzenesulfonate ester **1e** was prepared by reaction of 1,1-diphenylethanol (1 equiv) and freshly distilled triethylamine (2.5 equiv) with 4-nitrobenzenesulfonyl chloride (1.1 equiv) in anhydrous CH_2Cl_2 at -78°C , according to a previously described procedure.²⁰ The crude product was purified by column chromatog-

(26) See ref 25, pp 462–463.

raphy (silica gel; eluent hexane/CH₂Cl₂ 1:1) and identified by ¹H NMR and ¹³C NMR. ¹H NMR (CD₃CN): δ 8.14–8.11 (m, 2H), 7.44–7.31 (m, 12H), 1.99 (s, 3H). ¹³C NMR (CD₃CN): δ 152.6, 144.8, 128.2, 127.8, 126.7, 123.9, 120.8, 117.3, 89.7, 24.6.

Laser Flash Photolysis Studies. Laser flash photolysis experiments were carried out with a laser kinetic spectrometer using the fourth harmonic (266 nm) or the third harmonic (355 nm) of a Q-switched Nd:YAG laser. The laser energy was adjusted to ≤ 10 mJ/pulse by the use of the appropriate filter. A 3-mL Suprasil quartz cell (10 mm × 10 mm) was used and all experiments were carried out at $T = 22 \pm 0.5$ °C under magnetic stirring. When method 1 was employed, argon saturated solutions of the peroxides **1p** and **2p** ($\approx 2 \times 10^{-3}$ M, $A_{266} \approx 1.0$) in MeCN, MeCN/H₂O 1:1, TFE, or CH₂Cl₂ were photolyzed with 266 nm laser light. When method 2 was employed, argon or oxygen saturated solutions of 4-nitrobenzenesulfonate ester **1e** ($\approx 8 \times 10^{-5}$ M, $A_{355} \approx 1.0$) in MeCN, CCl₄, or benzene were

photolyzed with 355 nm laser light. Rate constants were obtained by averaging at least eight values and were reproducible to within 10%. The stability of the solution to the experimental conditions was checked spectrophotometrically by comparing the spectrum of the solution before irradiation with that obtained after irradiation.

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