The Effect of Ring Substitution on the *O*-Neophyl Rearrangement of 1,1-Diarylalkoxyl Radicals. A Product and Time-Resolved Kinetic Study

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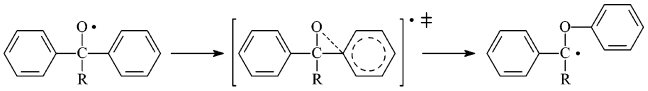
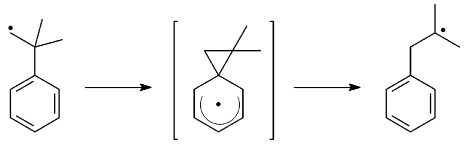


A product and time-resolved kinetic study of the effect of ring substitution on the reactivity of 1,1-diarylalkoxyl radicals has been carried out. The radicals undergo an *O*-neophyl shift to give the isomeric 1-aryl-1-aryloxyalkyl radicals from which the corresponding aromatic ketones are formed. The rearrangement rate constants are influenced by ring substitution, increasing in the presence of electron-withdrawing substituents and decreasing in the presence of electron-donating ones. From the results of product and kinetic studies, the following migratory aptitudes have been obtained: 4-trifluoromethylphenyl > phenyl ≅ 4-methylphenyl > 4-methoxyphenyl. Excellent Hammett-type correlations between the σ^+ substituent constants and both the visible absorption band maxima and the rearrangement rate constants have been obtained. The experimental results indicate that the rearrangement is governed by electronic effects in the starting 1,1-diarylalkoxyl radicals, whereas the stability of the rearranged carbon-centered radical plays a minor role, in line with a reactant-like transition state, strongly supporting the hypothesis that the *O*-neophyl rearrangement of 1,1-diarylalkoxyl radicals proceeds through a concerted mechanism.

The 1,2-migration of an aryl group in free radicals, known as the neophyl rearrangement, has been the subject of several studies.[2] This process is believed to occur via a spiro[2,5]octadienyl radical intermediate as shown in Scheme 1. However, despite these studies the mechanism of the neophyl rearrangement is still not entirely understood, the main question being whether the bridged radical is an intermediate or a transition state in this process.[2]

What concerns alkoxyl radicals instead is an analogous *O*-neophyl (or neophyl-like) rearrangement leading to an isomeric carbon-centered radical that has been observed only for radicals bearing at least two aryl substituents, such as the triphenylmethoxyl and 1,1-diphenylethoxyl radicals.[2−4] By analogy, the rearrangement is believed to occur via a 1-oxaspiro[2,5]octadienyl radical (Scheme 2).

SCHEME 1



Recently, on the basis of the results of laser flash photolysis experiments and AM1-UHF calculations, Banks and Scaiano proposed that the 1-oxaspiro[2,5]octadienyl radical is a true intermediate in the neophyl-like rearrangement of the 1,1-diphenylethoxyl radical.[5] The decay kinetics of the 1,1-diphenylethoxyl radical were found to match the formation kinetics of the rearranged 1-phenoxy-1-phenylethyl radical, leading to the suggestion that the lifetime of the bridged radical intermediate must be significantly smaller than 100 ns.

More recently, Grossi and Strazzari provided, via EPR spectroscopy, evidence for the involvement of a 1-oxaspiro-

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(1) (a) Università "Tor Vergata". (b) Università "La Sapienza".

(2) For an excellent review on radical aryl migration reactions, see: Studer, A.; Bossart, M. *Tetrahedron* **2001**, *57*, 9649−9667.

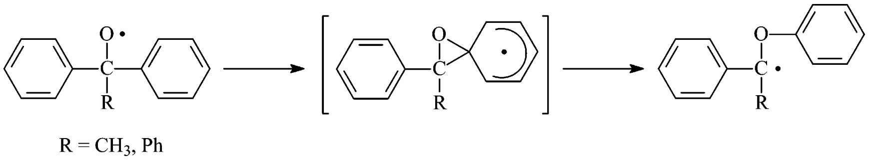
(3) Falvey, D. E.; Khambatta, B. S.; Schuster, G. B. *J. Phys. Chem.* **1990**, *94*, 1056−1059.

(4) For alkoxyl radicals bearing a single phenyl substituent such as the benzyloxyl and cumyloxyl radicals, aryl migration would lead to carbon-centered radicals that are significantly less stable than those formed from both the 1,1-diphenylethoxyl and triphenylmethoxyl radicals. Accordingly, with the former radicals the 1,2-phenyl shift does not compete with hydrogen atom abstraction, and β-fragmentation reactions.

(5) Banks, J. T.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 3527−3531.

10.1021/jo0502448 CCC: $30.25

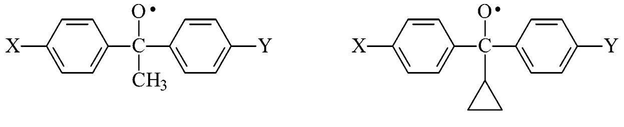
SCHEME 2



[2,5]octadienyl radical as an intermediate in the rearrangement of both the 1,1-diphenylethoxyl and the triphenylmethoxyl radicals.[6] The alkoxyl radicals were generated by photolysis of the parent alcohols in the presence of ceric ammonium nitrate (CAN). Quite interestingly, in the same study no evidence was obtained for the formation of a bridged radical but only of a peroxyl radical when the 1,1-diphenylethoxyl radical was generated by photolysis of the parent 1,1-diphenylethyl peroxide.[7] It was proposed that CAN plays a key role in the formation and stabilization of the bridged radical intermediate: the coordination of the alcoholic oxygen to the ceric ion increases the electrophilicity of this group favoring the cyclization process. This is an observation that, however, raises some doubt on the involvement of free alkoxyl radicals in the CAN-induced photooxidation of arylcarbinols, indicating that the mechanism of the neophyl-like rearrangement of alkoxyl radicals is also still not entirely understood and that additional information in this respect is certainly needed.

In this context, product studies have also shown that in the rearrangement of triarylmethoxyl radicals the product distributions can be influenced by the presence of ring substituents. Thus, products deriving from the migration of both the 4-nitrophenyl and 4-benzoylphenyl groups in (4-nitrophenyl)diphenylmethoxyl and (4-benzoylphenyl)diphenylmethoxyl radicals, respectively, were formed in greater amounts than those deriving from the migration of the unsubstituted phenyl group;[8−10] whereas the 4-methylphenyl group showed a similar migratory aptitude as that of the phenyl group.[11] These results have been interpreted in terms of the activation toward intramolecular free radical attack exerted by the presence of ring substituents. A similar activation was predicted in the presence of methoxy ring substituents,[8,12] but unfortunately no clear information in this respect is available.[9] These findings also suggest that the rates of 1,2-aryl shift are expected to be influenced by ring substitution. Along these lines, it seemed particularly interesting to study the effect of both electron-withdrawing and electron-releasing ring substituents on the reactivity of 1,1-diarylalkoxyl radicals. For this purpose, we have carried out product and time-resolved kinetic studies on the reactivity of 1,1-diarylethoxyl radicals **1**$^{\bullet}$−**3**$^{\bullet}$ and cyclopropyldiarylmethoxyl radicals **4**$^{\bullet}$−**8**$^{\bullet}$ (Chart 1). The use of the cyclopropyl derivatives is a consequence of the instability of both 1-(4-methoxyphenyl)-1-phenylethanol and 1,1-di(4-methoxyphenyl)ethanol, which undergo water elimination very easily.[13] Cyclopropyl(4-methoxyphenyl)phenylmethanol (**5a**) and cyclopropyl[bis(4-methoxyphenyl)]methanol (**6a**) (precursors of radicals **5**$^{\bullet}$ and **6**$^{\bullet}$) are instead stable under the experimental conditions employed.

CHART 1



1$^{\bullet}$: X = Y = H
2$^{\bullet}$: X = H; Y = CH_3
3$^{\bullet}$: X = Y = CH_3

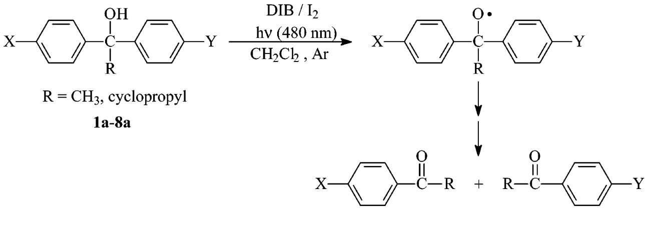
4$^{\bullet}$: X = Y = H
5$^{\bullet}$: X = H; Y = OCH_3
6$^{\bullet}$: X = Y = OCH_3
7$^{\bullet}$: X = H; Y = CF_3
8$^{\bullet}$: X = Y = CF_3

As a matter of completeness, product studies have been carried out for all the 1,1-diarylalkanols (**1a**−**8a**: precursors of the 1,1-diarylalkoxyl radicals **1**$^{\bullet}$−**8**$^{\bullet}$), even though the reactions of symmetric substrates **1a**, **3a**, **4a**, **6a**, and **8a** do not provide information on the effect of ring substituents.

Results

Product Studies. The 1,1-diarylalkoxyl radicals **1**$^{\bullet}$−**8**$^{\bullet}$ have been generated photochemically by visible light irradiation of CH_2Cl_2 solutions containing the parent 1,1-diarylalkanol (**1a**−**8a**), (diacetoxy)iodobenzene (DIB) and I_2. It is well established that under these conditions the DIB/I_2 reagent converts alcohols into intermediate hypoiodites,[14] which are then photolyzed to give alkoxyl radicals, precursors of the observed reaction products.[15−17] With 1,1-diarylalkanols, the corresponding alkoxyl radicals so formed are expected to rearrange to give isomeric carbon-centered radicals, from which, after efficient iodine trapping,[18,19] the product alkyl aryl ketones are formed (Scheme 3).

SCHEME 3



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[6] Grossi, L.; Strazzari, S. *J. Org. Chem.* **2000**, *65*, 2748−2754.

[7] In this EPR experiment, carried out in N_2-saturated MeCN solution at 230 K, the peroxyl radical is described to be formed by oxygen quenching of either the bridged radical or the rearranged 1-phenoxy-1-phenylethyl radical. However, due to the very short lifetime suggested for the former radical (see ref 5), quenching of this radical by *traces* of oxygen is expected to be slower than the formation of the 1-phenoxy-1-phenylethyl radical. As a consequence, the peroxyl radical (if formed) is likely to derive from the reaction of this radical with oxygen.

[8] Bartlett, P. D.; Cotman, J. D., Jr. *J. Am. Chem. Soc.* **1950**, *72*, 3095−3099.

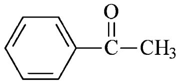
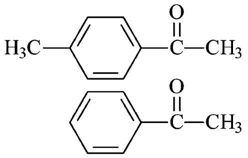
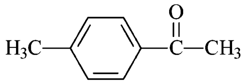
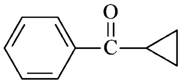
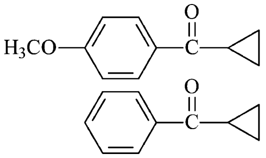
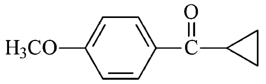
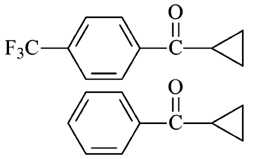
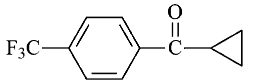
[9] (a) Starnes, W. H., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1807−1815. (b) Starnes, W. H., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 3368−3369.

[10] Neckers, D. C.; Linden, S.-M.; Williams, B. L.; Zakrzewski, A. *J. Org. Chem.* **1989**, *54*, 131−135.

[11] Kharasch, M. S.; Poshkus, A. C.; Fono, A.; Nudenberg, W. *J. Org. Chem.* **1951**, *16*, 1458−1470.

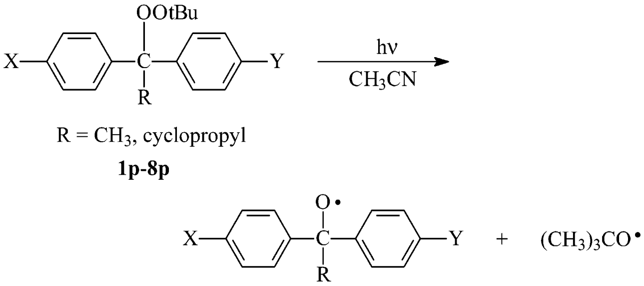
[12] Kamata, M.; Komatsu, K. *Tetrahedron Lett.* **2001**, *42*, 9027−9030.

TABLE 1. Yields and Product Distributions (Q)[a] Observed after Irradiation of Argon-Saturated CH_2Cl_2 Solutions Containing 1,1-Diarylalkanols 1a−8a, DIB, and I_2[b]

substrate	products	Q	yield (%)
1a		-	27
2a		1.05[c]	41
3a		-	37
4a		-	33
5a		1.64[c]	39
6a		-	39
7a		0.54	23[d]
8a		-	9[e]

[a] Molar ratio between ring-substituted and unsubstituted alkyl aryl ketone. [b] [DIB] = 22 mM, [I_2] = 10 mM, [substrate] = 10 mM, irradiation wavelength = 480 nm, irradiation time = 15 min, T = 20 °C. [c] No significant variation of Q was observed after 30 min of irradiation. [d] Irradiation time = 10 min. [e] Irradiation time = 5 min. At longer irradiation times, formation of an unidentified product was observed.

SCHEME 4



Argon-saturated CH_2Cl_2 solutions containing the 1,1-diarylalkanol (**1a**−**8a**) (10 mM), DIB (11−40 mM), and I_2 (10−40 mM) were irradiated with visible light ($\lambda_{max} \approx$ 480 nm) at T = 20 °C for 15 min. The irradiation time was chosen in such a way as to avoid complete substrate conversion. After workup, the reaction products were identified by GC (comparison with authentic samples) and GC−MS and quantitatively determined, together with the unreacted substrate, by GC using bibenzyl as internal standard. The reaction of 1,1-diphenylethanol (**1a**) was carried out under a variety of experimental conditions (see Supporting Information), leading in all cases to the formation of acetophenone as the exclusive product.[20] Convenient experimental conditions were found using a 2.2:1:1 DIB/I_2/**1a** ratio, and analogous conditions were thus employed for the reactions of 1,1-diarylalkanols **2a**−**8a**. The product yields observed after irradiation of argon-saturated CH_2Cl_2 solutions containing substrates **1a**−**8a**, DIB, and I_2 are collected in Table 1.

In the same table, the product distributions, expressed in terms of the molar ratios (Q) of ring-substituted and unsubstituted acetophenones or aryl cyclopropyl ketones observed in the reactions of nonsymmetric 1,1-diarylalkanols **2a**, **5a**, and **7a**, are also reported.

With substrates **1a**, **3a**, **4a**, **6a**, and **8a**, exclusive formation of the corresponding acetophenone or aryl cyclopropyl ketone was observed. The reactions of nonsymmetric 1,1-diarylalkanols **2a**, **5a**, and **7a** led instead to the formation of both the unsubstituted and ring-substituted ketone. In particular, the reaction of **2a** led to the formation of comparable amounts of 4-methylacetophenone and acetophenone (Q = 1.05). Cyclopropyl 4-methoxyphenyl ketone was instead the major reaction product observed in the reaction of **5a** accompanied by cyclopropyl phenyl ketone (Q = 1.64), whereas with **7a** cyclopropyl phenyl ketone was the major reaction product accompanied by cyclopropyl 4-trifluoromethylphenyl ketone (Q = 0.54).

Time-Resolved Studies. The 1,1-diarylalkoxyl radicals $1^{\bullet}$−$8^{\bullet}$ have been generated in MeCN by 266-nm laser flash photolysis (LFP) of the parent *tert*-butyl peroxides **1p**−**8p** (Scheme 4), which in turn have been synthesized by reaction of 1,1-diarylalkanols **1a**−**8a** with *tert*-butyl hydroperoxide in the presence of *p*-toluenesulfonic acid according to a slight modification of a previously described procedure (see Supporting Information).[21,22]

All the alkoxyl radicals display a broad absorption band in the visible region of the spectrum, which is unaffected by oxygen and whose position and intensity is influenced by the presence of ring substituents falling between 490 and 640 nm, in line with previous observations on the spectral properties of ring-substituted arylcarbinyloxyl radicals.[22−24] The visible absorption band was observed to decay in the nanosecond to microsecond

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(13) Grummitt, O.; Marsh, D. *J. Am. Chem. Soc.* **1948**, *70*, 1289−1290.

(14) Courtneidge, J. L.; Lusztyk, J.; Pagè, D. *Tetrahedron Lett.* **1994**, *35*, 1003−1006.

(15) Aureliano Antunes, C. S.; Bietti, M.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2004**, *69*, 5281−5289.

(16) Suárez, E.; Rodriguez, M. S. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 2, pp 440−454.

(17) Togo, H.; Katohgi, M. *Synlett* **2001**, *5*, 565−581.

(18) Minisci, F.; Recupero, F.; Gambarotti, C.; Punta, C.; Paganelli, R. *Tetrahedron Lett.* **2003**, *44*, 6919−6922.

(19) Hook, S. C. W.; Saville, B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 589−593.

(20) No evidence for the formation of phenols was obtained in the product analysis experiments.

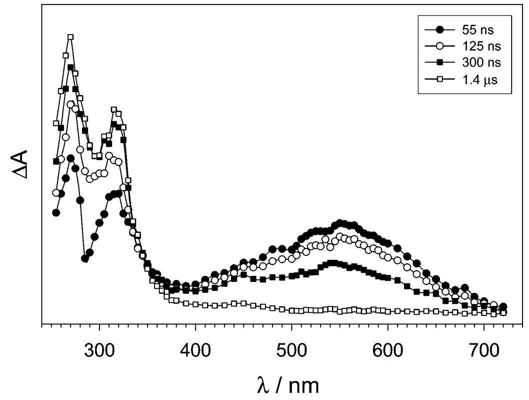

FIGURE 1. Time-resolved absorption spectra observed after 266-nm LFP of **3p** (1.8 mM) in an argon-saturated MeCN solution at 55 ns (●), 125 ns (○), 300 ns (■), and 1.4 μs (□) after the 8-ns, 10 mJ laser pulse.

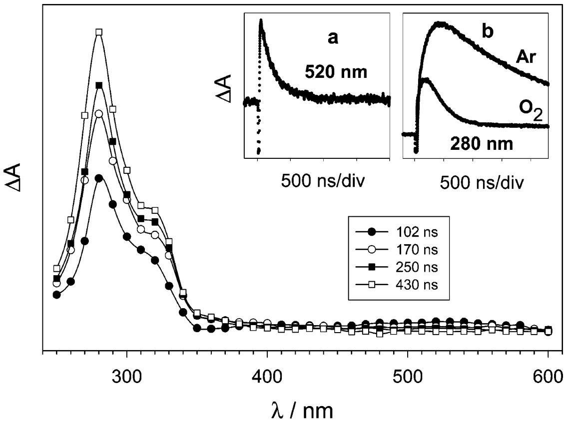

FIGURE 2. Time-resolved absorption spectra observed after 266-nm LFP of **7p** (1.67 mM) in an argon-saturated MeCN solution at 102 (●), 170 (○), 250 (■), and 430 ns (□) after the 8-ns, 10 mJ laser pulse. Insets: (a) First-order decay of radical $7^\bullet$ monitored at 520 nm and (b) corresponding first-order buildup of absorption at 280 nm, measured under argon and oxygen.

time scale depending on ring substitution, leading in all 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-diarylalkoxyl radical.[3,5,24]

As an example, Figure 1 displays the time-resolved spectra observed after LFP of an argon-saturated MeCN solution containing peroxide **3p**, showing after 55 ns (filled circles) a broad absorption band centered at 550 nm, which is assigned to the radical $\mathbf{3}^\bullet$.

This species undergoes a first-order decay that is accompanied by a corresponding buildup of optical density at 260 and 320 nm assigned to the 1-(4-methylphenoxy)-1-(4-methylphenyl)ethyl radical (an isosbestic point is visible at 345 nm). As expected for a carbon-centered radical, a rapid decay of the 260- and 320-nm bands was observed in the presence of oxygen.

Figure 2 displays instead the time-resolved absorption spectra observed after LFP of an argon-saturated MeCN solution containing peroxide **7p**. The spectrum recorded after 102 ns (filled circles) shows a very weak absorption band centered at 520 nm, which is assigned to the radical $\mathbf{7}^\bullet$. This species undergoes a first-order decay (inset a), accompanied by a corresponding buildup of optical density at 280 nm (an isosbestic point is visible at 380 nm) whose decay is significantly accelerated in the presence of oxygen (inset b), which again is assigned to the rearranged carbon-centered radical(s).

TABLE 2. Visible Absorption Band Maximum Wavelengths and Decay Rate Constants for 1,1-Diarylalkoxyl Radicals $\mathbf{1}^\bullet$–$\mathbf{8}^\bullet$ Measured in Argon-Saturated MeCN Solution at T = 22 °C

radical	$\lambda_{\max}$ (vis)/nm[a]	k/s^{-1} [b,c]
$\mathbf{1}^\bullet$	535	2.8×10^6
$\mathbf{2}^\bullet$	540	2.4×10^6
$\mathbf{3}^\bullet$	550	2.0×10^6
$\mathbf{4}^\bullet$	535	2.0×10^6
$\mathbf{5}^\bullet$	610	5.1×10^5
$\mathbf{6}^\bullet$	640	2.6×10^5
$\mathbf{7}^\bullet$	520	5.0×10^6
$\mathbf{8}^\bullet$	490	1.8×10^7

[a] Visible absorption band maximum of the 1,1-diarylalkoxyl radical. [b] Measured following the decay of the 1,1-diarylalkoxyl radical at the visible absorption maximum. [c] The decay rate constants were not affected by the presence of oxygen.

The decay of the 1,1-diarylethoxyl radicals ($\mathbf{1}^\bullet$–$\mathbf{3}^\bullet$) and cyclopropyldiarylmethoxyl radicals ($\mathbf{4}^\bullet$–$\mathbf{8}^\bullet$) 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 rate constants thus obtained are reported in Table 2 together with the visible absorption band maximum wavelengths of the 1,1-diarylalkoxyl radicals $\mathbf{1}^\bullet$–$\mathbf{8}^\bullet$.

Discussion

The results of product studies collected in Table 1 show that the reactions of 1,1-diarylalkoxyl radicals lead to the exclusive formation of acetophenones or aryl cyclopropyl ketones. In particular, with nonsymmetric 1,1-diarylalkanols **2a**, **5a**, and **7a**, formation of both the unsubstituted and ring-substituted ketone was observed. Formation of these products can be rationalized in terms of the competition between the two possible 1,2-aryl shifts in the intermediate 1,1-diarylalkoxyl radicals (paths a and b in Scheme 5: R = Me, cyclopropyl).

Quite interestingly, when R = cyclopropyl (substrates **4a**–**8a**) the 1,2-aryl shift leads to the formation of a 1,1-disubstituted cyclopropylcarbinyl radical. The exclusive formation of aryl cyclopropyl ketones in the reactions of these substrates clearly indicates that iodine trapping of the rearranged radical occurs significantly faster than cyclopropyl ring opening, in agreement with the relatively low rate constants measured for ring opening of α-phenyl-substituted cyclopropylcarbinyl radicals.[25] Moreover, in the reactions of substrates **4a**–**8a** no β-scission of the C-cyclopropyl bond in the corresponding alkoxyl radicals

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(21) Hendrickson, W. H.; Nguyen, C. C.; Nguyen, J. T.; Simons, K. T. *Tetrahedron Lett.* **1995**, *36*, 7217–7220.

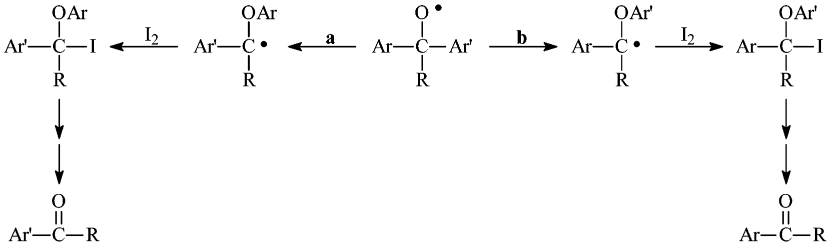
(22) Baciocchi, E.; Bietti, M.; Salamone, M.; Steenken, S. *J. Org. Chem.* **2002**, *67*, 2266–2270.

(23) Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576–6577.

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

(25) Halgren, T. A.; Roberts, J. D.; Horner, J. H.; Martinez, F. N.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **2000**, *122*, 2988–2994.

SCHEME 5



$4^\bullet$–$8^\bullet$ occurs, as shown by the absence of diaryl ketones among the reaction products. This result is in line with the relatively low stability of the cyclopropyl radical.[26–28]

The results collected in Table 1 show that while the 4-methylphenyl and phenyl groups are characterized by a similar migratory aptitude ($\boldsymbol{Q}$ = 1.05), in agreement with the results of previous studies,[11] opposite behaviors are instead observed in the presence of methoxy (**5a**) or trifluoromethyl (**7a**) ring substituents: the phenyl group migrates better than the 4-methoxyphenyl one ($\boldsymbol{Q}$ = 1.64) while 4-trifluoromethylphenyl migrates better than phenyl ($\boldsymbol{Q}$ = 0.54). This behavior is in contrast with the predicted activation toward intramolecular free radical attack exerted by the presence of both electron-withdrawing and electron-releasing ring substituents.[8,12]

A possible explanation for this behavior may be that the reaction is influenced by the stability of the rearranged carbon-centered radical. Along this line, it is well-known that a methoxy substituent stabilizes carbon-centered radicals, whereas the presence of a trifluoromethyl one determines a slight destabilization, as clearly shown for example for benzyl and methyl radicals.[29–33] Accordingly, the product distributions observed in the reactions of radicals **5a** and **7a** would indicate in both cases preferential formation of the most stable carbon-centered radical: the (4-methoxyphenyl)phenoxycyclopropylcarbinyl radical over the (4-methoxyphenoxy)phenylcyclopropylcarbinyl one from **5a**, and the phenyl(4-trifluoromethylphenoxy)cyclopropylcarbinyl radical over the phenoxy-(4-trifluoromethylphenyl)cyclopropylcarbinyl one from **7a**. However, the experimental rate constants displayed in Table 2 showing that the trifluoromethyl substituted radicals $7^\bullet$ and $8^\bullet$ are significantly more reactive than the methoxy substituted ones $5^\bullet$ and $6^\bullet$, and in particular that $8^\bullet$ is more reactive than $7^\bullet$ whereas $6^\bullet$ is less reactive than $5^\bullet$, are in sharp contrast with this hypothesis. From these resuts, it can be reasonably concluded that, in the *O*-neophyl rearrangement of 1,1-diarylalkoxyl radicals, the stability of the rearranged carbon-centered radical is not important, an observation that points toward a transition state of the rearrangement rate-determining step where radical-stabilizing effects play a minor role. In other words, the transition state must be characterized by a small degree of carbon radical character.

The spectral data collected in Table 2 confirm that the position of the visible absorption band of arylcarbinyloxyl radicals is red-shifted by electron-donating ring substituents and blue-shifted by electron-withdrawing ones, as previously shown for ring-substituted cumyloxyl radicals.[22–24] An excellent Hammett-type correlation between the experimentally measured excitation energies corresponding to the visible absorption maxima of cyclopropyldiarylmethoxyl radicals $4^\bullet$, $6^\bullet$, and $8^\bullet$ and the σ^+ substituent constants is obtained (Figure 3), in line with that observed previously for ring-substituted cumyloxyl radicals.[22]

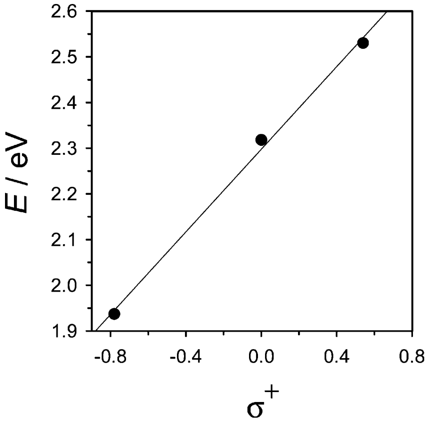


FIGURE 3. Hammett-type correlation between the experimentally measured energies at the visible absorption maxima of radicals $4^\bullet$, $6^\bullet$, and $8^\bullet$ and σ^+ substituent constants. From the linear regression: slope = 0.45 eV^{-1}, r^2 = 0.9966.

In this connection, it has been recently suggested that arylcarbinyloxyl radicals are characterized by a certain degree of internal charge transfer, with the aromatic ring bearing a partial positive charge and the oxygen atom a partial negative one;[23] the visible absorption band of arylcarbinyloxyl radicals has been attributed to a $\pi \rightarrow \pi^*$ transition, which determines an increase in the extent of charge separation in the radical on going from the ground state to the excited state.[22,23]

This charge separation may be reasonably rationalized in terms of the contribution of negative hyperconjugation structures, such as those shown in Scheme 6, to the stability of the starting arylcarbinyloxyl radical.

What concerns the kinetic data instead is the rate constant measured for the decay of the 1,1-diphenylethoxyl radical ($1^\bullet$) to give the 1-phenoxy-1-phenylethyl radical, $k = 2.8 \times 10^6$ s^{-1}, which is very similar to those measured previously for the same radical.[3,5,24] The observation that

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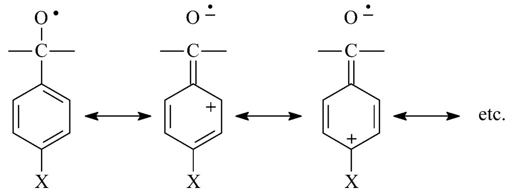
SCHEME 6



the rate constant measured for decay of the cyclopropyldiphenylmethoxyl radical (**4**$^{\bullet}$), $k = 2.0 \times 10^6$ s^{-1}, is comparable with that measured for **1**$^{\bullet}$, indicates that replacement of the methyl group with a cyclopropyl one has only a negligible effect on the reactivity of these radicals.

In contrast with the results obtained for the β-scission of ring-substituted cumyloxyl radicals, where the rate constants were found to be essentially independent from the nature of the substituent,[22] with 1,1-diarylalkoxyl radicals the decay rate constants are significantly influenced by ring substitution. Accordingly, as compared to the unsubstituted radicals **1**$^{\bullet}$ and **4**$^{\bullet}$, an increase in rate is observed in the presence of electron-withdrawing substituents while the presence of electron-donating ones determines a rate decrease, with radical **1**$^{\bullet}$ reacting at a slightly higher rate than **3**$^{\bullet}$ and radicals **6**$^{\bullet}$, **4**$^{\bullet}$, and **8**$^{\bullet}$ displaying the following relative reactivities: 0.13:1:9. This reactivity order is in agreement with the results of product studies described above for the nonsymmetric substrates **2a**, **5a**, and **7a** and from which the following migratory aptitudes can be derived: 4-trifluoromethylphenyl > phenyl ≅ 4-methylphenyl > 4-methoxyphenyl.

Quite importantly, a good Hammett-type correlation is also obtained between the experimental rate constants measured for the rearrangement of cyclopropyldiarylmethoxyl radicals **4**$^{\bullet}$, **6**$^{\bullet}$, and **8**$^{\bullet}$ and the σ^+ substituent constants (Figure 4), in line with that observed for the visible absorption maxima of the same radicals shown in Figure 3.

This observation provides additional support to the hypothesis of the existence of an internal charge transfer in the ground state of 1,1-diarylalkoxyl radicals, indicating moreover that efficient stabilization of the partial positive charge is also responsible for the effect of ring substitution on the rearrangement rate constants. In particular, the observation of a positive slope is in line with a reaction that involves a decrease in the extent of positive charge on the aromatic ring on going from the starting 1,1-diarylalkoxyl radical to the transition state.

By combining the ***Q*** ratios measured for the reactions of 1,1-diarylalkanols **5a** and **7a** reported in Table 1 with the decay rate constants measured for cyclopropyldiarylmethoxyl radicals **4**$^{\bullet}$, **5**$^{\bullet}$, and **7**$^{\bullet}$ reported in Table 2, we can obtain the partial rate constants for migration of the unsubstituted (k_{H}) and 4-X substituted ring (k_{X}: X = H, OMe, CF$_3$). These data are collected in Table 3.

The partial rate constants indicate that the presence of the ring substituent influences the migration rate of both aromatic rings in the 1,1-diarylalkoxyl radical. Thus, as compared to **4**$^{\bullet}$, migration of the unsubstituted ring is favored by the presence of a trifluoromethyl substituent as in **7**$^{\bullet}$ and disfavored by the presence of a methoxy substituent as in **5**$^{\bullet}$.

Again, excellent Hammett-type correlations between the partial rate constants for migration of the 4-X substituted and unsubstituted rings in cyclopropyldiarylmethoxyl radicals **4**$^{\bullet}$, **5**$^{\bullet}$, and **7**$^{\bullet}$ and σ^+ substituent constants are obtained (see Figure S1 in the Supporting Information, plots a and b, respectively). The small ρ values (0.93 and 0.56, respectively) are in agreement with reactions involving little charge separation. Comparison between these values indicates, as expected, that migration of the 4-X substituted ring is more sensitive to substituent effects than migration of the unsubstituted one.

Quite interestingly, Beckwith observed that the neophyl rearrangement of alkenylaryl radicals is favored by the presence of electron-withdrawing substituents on the migrating aromatic ring,[34] a behavior that is similar to that observed in the present case and that was rationalized in terms of the nucleophilic character of alkyl radicals. However in this study, rather than simply invoking an *unexpected* nucleophilic character for the 1,1-diarylalkoxyl radicals, the experimental results discussed above seem more in line with the hypothesis that stabilizing effects on the starting 1,1-diarylalkoxyl radical, expressed in terms of the negative hyperconjugation contributions described in Scheme 6, play an important role.[35] According to this picture, in a nonsymmetric 1,1-diarylalkoxyl radical, the oxygen radical will preferentially attack the aromatic ring that is less involved in the resonance stabilization, that is, the ring characterized by the smallest extent of hyperconjugation: a hypothesis

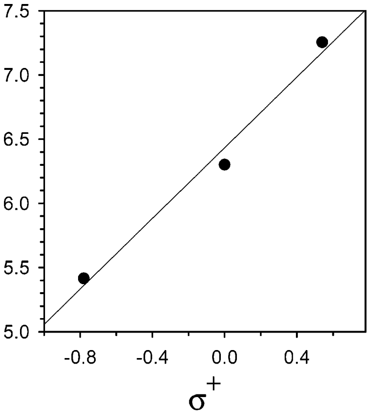


FIGURE 4. Hammett-type correlation between the experimental rate constants measured for the rearrangement of cyclopropyldiarylmethoxyl radicals **4**$^{\bullet}$, **6**$^{\bullet}$, and **8**$^{\bullet}$ and the σ^+ substituent constants. From the regression analysis: $\rho = 1.38$; $r^2 = 0.984$.

TABLE 3. Partial Rate Constants for the Migration of the Unsubstituted and 4-X Substituted Ring in Cyclopropyldiarylmethoxyl Radicals 4$^{\bullet}$, 5$^{\bullet}$, and 7$^{\bullet}$

radical	***Q***[a]	k/s^{-1} [b]	k_{H}/s^{-1} [c]	k_{X}/s^{-1} [d]
4$^{\bullet}$	–	2.0×10^6	1.0×10^6	1.0×10^6
5$^{\bullet}$	1.64	5.1×10^5	3.2×10^5	1.9×10^5
7$^{\bullet}$	0.54	5.0×10^6	1.75×10^6	3.25×10^6

[a] Molar ratio between ring-substituted and unsubstituted aryl cyclopropyl ketone (see Table 1). [b] Measured following the decay of the 1,1-diarylalkoxyl radical at the visible absorption maximum (see Table 2). [c] Rate constant for migration of the unsubstituted ring. [d] Rate constant for migration of the 4-X (X = H, OMe, CF$_3$) substituted ring.

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SCHEME 7

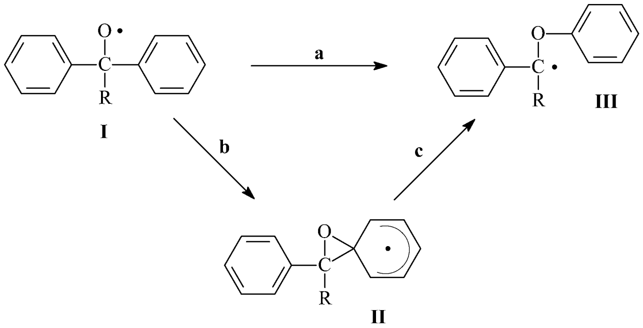
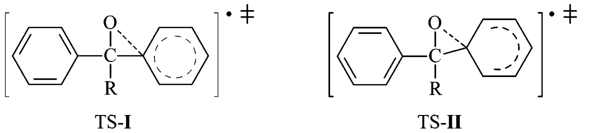


CHART 2



that fully accounts for the results of kinetic and product studies. In addition, the reactivity order observed in the series of the symmetric cyclopropyldiarylmethoxyl radicals **4**$^•$, **6**$^•$, and **8**$^•$ (**8**$^•$ > **4**$^•$ > **6**$^•$) reflects their differences in stability, which, accordingly, are expected to follow the opposite order (**6**$^•$ > **4**$^•$ > **8**$^•$), with the ring-dimethoxylated radical **6**$^•$ characterized by the greatest extent of resonance stabilization.

It is thus possible to discuss the results of product and time-resolved kinetic studies described above in terms of the two possible mechanisms proposed previously for the *O*-neophyl rearrangement of the 1,1-diphenylethoxyl radical (Scheme 7, R = Me, cyclopropyl, showing for the sake of simplicity a ring-unsubstituted radical):[2] the stepwise mechanism, proceeding through the formation of a bridged 1-oxaspiro[2,5]octadienyl radical intermediate (paths b and c), and the concerted mechanism (path a).

In a stepwise mechanism, by reasonably assuming that the first step is the rate-determining one[5] and by considering that the rearranged benzyl radical (**III**) is significantly more stable than the parent 1,1-diarylalkoxyl radical (**I**), the bridged 1-oxaspiro[2,5]octadienyl radical intermediate (**II**) is expected to be at a relatively higher energy than **I**.[5,36] Thus, as a consequence of the Hammond postulate,[37] the transition state of the rate-determining step will be close in structure to radical **II**, exhibiting a pronounced cyclohexadienyl radical character (Chart 2, TS-**II**). On the other hand, in a concerted mechanism a reactant-like transition state that is close in structure to radical **I**, displaying a certain extent of charge separation and a limited cyclohexadienyl radical character, is to be expected, a transition state where formation of a new bond by attack of the oxygen radical onto the aromatic ring has not proceeded significantly (Chart 2, TS-**I**). This picture is clearly more in line with the experimental evidences presented above.[38]

This hypothesis is in contrast with the suggestion of Banks and Scaiano that the 1-oxaspiro[2,5]octadienyl radical is a true intermediate in the neophyl-like rearrangement of the 1,1-diphenylethoxyl radical.[5] In this context, it is important to point out that this suggestion was not supported by any direct experimental evidence but only by the results of AM1-UHF calculations, which, however, are not expected to provide sufficiently reliable results. Unfortunately, theoretical calculations carried out at a higher lever of theory, which may provide additional information on the mechanism of the *O*-neophyl rearrangement of 1,1-diarylalkoxyl radicals, are not presently available.

In conclusion, the results of product and time-resolved kinetic studies on the *O*-neophyl rearrangement of ring-substituted 1,1-diarylalkoxyl radicals strongly support the hypothesis that the reaction proceeds through a concerted mechanism and not via formation of an intermediate 1-oxaspiro[2,5]octadienyl radical as previously proposed.[3,5,6] The rearrangement is governed by electronic effects in the starting 1,1-diarylalkoxyl radicals, explained in terms of negative hyperconjugative contributions, whereas the stability of the rearranged carbon-centered radical plays a minor role.

Experimental Section

Materials. Spectroscopic-grade MeCN was used as received. CH_2Cl_2 was purified prior to use by column chromatography over basic alumina. (Diacetoxy)iodobenzene (DIB), iodine, 1,1-diphenylethanol (**1a**), cyclopropyldiphenylmethanol (**4a**), and cyclopropyl-4-methoxydiphenylmethanol (**5a**) were of the highest commercial quality available and were used as received. Details of the synthesis of 1,1-diarylalkanols **2a**, **3a**, **6a**−**8a**, the *tert*-butyl 1,1-diarylethyl peroxides (**1p**−**3p**), and *tert*-butyl cyclopropyldiarylmethyl peroxides (**4p**−**8p**) are given in the Supporting Information. The purity of the 1,1-diarylalkanols (**1a**−**8a**) employed in the product studies was always ≥99%.

Product Analysis. All the reactions were carried out under an argon atmosphere. Irradiations were performed with visible light (10 × 15 W lamps with emission between 400 and 550 nm, $\lambda_{max} \approx 480$ nm). The reactor was a cylindrical flask equipped with a water cooling jacket thermostated at $T = 20$ °C. Irradiation times were chosen in such a way as to avoid complete substrate consumption. In a typical experiment, a solution of the alcohol (10 mM) in CH_2Cl_2 (5 mL) containing (diacetoxy)iodobenzene (22 mM) and iodine (10 mM) was irradiated for times ranging between 5 and 60 min under Ar bubbling. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with a 10% aqueous thiosulfate solution (2 × 30 mL) and water (2 × 30 mL) and dried over anhydrous sodium sulfate. Reaction products and unreacted substrate were identified by GC−MS and quantitatively determined by GC using bibenzyl as internal standard. Good-to-excellent mass balances (≥85%) were obtained in all experiments.

Laser Flash Photolysis Studies. Laser flash photolysis experiments were carried out with a laser kinetic spectrometer using the fourth harmonic (266 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 for all experiments. Argon- or oxygen-saturated MeCN solutions of the peroxides **1p**−**8p** (between

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(35) According to this picture, the observation that the rate constants for β-scission of ring-substituted cumyloxyl radicals are essentially independent from the nature of the substituent (see ref 22) may indicate that substituent effects operate in the same direction on both the cumyloxyl radical and the product acetophenone.

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(38) As a consequence of a reactant-like transition state, possible differences in C−C_{Ar} BDE in the 1,1-diaryalkoxyl radicals determined by the presence of ring substituents should not be important.

5×10^{-4} and 3×10^{-3} M, $A_{266} \approx 1.0$) were used. All the experiments were carried out at $T = 22 \pm 0.5$ °C under magnetic stirring. Rate constants were obtained by averaging 4−8 values, each consisting of the average of at least three laser shots, and were reproducible to within 10%.

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Supporting Information Available: Details on the product studies and on the synthesis and characterization of the precursor 1,1-diarylalkanols and *tert*-butyl 1,1-diarylalkyl peroxides. Hammett-type correlations between the partial rate constants for radicals $\mathbf{4}^{\bullet}$, $\mathbf{5}^{\bullet}$, and $\mathbf{7}^{\bullet}$ and σ^{+} substituent constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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