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DFT Evidence for a Stepwise Mechanism in the *O*-Neophyl Rearrangement of 1,1-Diarylalkoxyl Radicals

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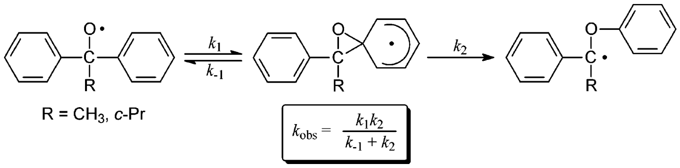
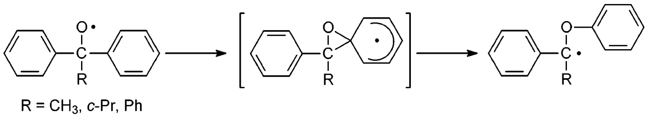


Hybrid DFT calculations of the potential energy surface (PES) relative to the *O*-neophyl rearrangement of a series of ring-substituted 1,1-diarylalkoxyl radicals have been carried out at the UB3LYP/6-31G(d) level of theory. On the basis of the computational data, the rearrangement can be described as a consecutive reaction of the type **a** ⇆ **b** → **c** (see above graphic), and the steady-state approximation could be applied in all cases to the intermediate **b**. The first-order rearrangement rate constants [$k_{obs} = k_1k_2/(k_{-1} + k_2)$] were thus obtained from the computed activation free-energies and were compared with the experimental rate constants measured previously in MeCN solution by laser flash photolysis. An excellent agreement is observed along the two series, which strongly supports the hypothesis that the *O*-neophyl rearrangement of 1,1-diarylalkoxyl radicals proceeds through the formation of the reactive 1-oxaspiro [2,5]octadienyl radical intermediate. This is in contrast to previous hypotheses that involve either a long-lived intermediate or the absence of this intermediate along the reaction path. The calculated rearrangement free-energies decrease upon going from the methoxy-substituted radical ($\Delta G° = -16.4$ kcal·mol^{-1}) to the nitro-substituted one ($\Delta G° = -21.8$ kcal·mol^{-1}), which follows a trend that is similar to the one observed for the $C_{Ar}-O$ bond dissociation enthalpies (BDEs) of ring-substituted anisoles. This evidence indicates that in the *O*-neophyl rearrangement the effect of ring substituents on the strength of the newly formed $C_{Ar}-O$ bond plays an important role.

Introduction

The 1,2-migration of an aryl group in arylcarbinyloxyl radicals, known as the *O*-neophyl (or neophyl-like) rearrangement, has been the subject of several studies.[1] This process converts an oxygen centered radical into an isomeric carbon centered radical, and it has been observed only for radicals that bear at least two α-aryl substituents, such as the triarylmethoxyl and 1,1-diarylalkoxyl radicals. The mechanism of this rearrangement is still not entirely understood; the main question is whether the bridged 1-oxaspiro[2,5]octadienyl radical is an intermediate or a transition-state in this process (Scheme 1).

SCHEME 1



Evidence in favor of the intermediacy of a 1-oxaspiro[2,5]-octadienyl radical was provided by Schuster[2] and Grossi[3] by means of laser flash photolysis (LFP) and EPR spectroscopy, respectively. After LFP of a MeCN solution containing *tert*-butyl 1,1-diphenylethylperoxide, Schuster observed the formation of a transient that was characterized by an absorption band centered at 535 nm and assigned this transient to the bridged radical.[2] Later, Scaiano showed by LFP studies that Schuster's assignment was not correct and reassigned the 535 nm transient to the 1,1-diphenylethoxyl radical (**1a**).[4,5] He further concluded that the bridged radical was either not an intermediate in the rearrangement of **1a** or was a short-lived intermediate that was not detectable with nanosecond LFP techniques. Grossi reported EPR spectra, which were obtained during a ceric ammonium nitrate (CAN) induced photooxidation of triphenylmethanol and

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[1] For an excellent review on radical aryl migration reactions, see Studer, A.; Bossart, M. *Tetrahedron* **2001**, *57*, 9649−9667.

[2] Falvey, D. E.; Khambatta, B. S.; Schuster, G. B. *J. Phys. Chem.* **1990**, *94*, 1056−1059.

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

[4] Banks, J. T.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 3527−3531.

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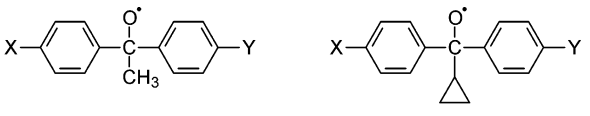
CHART 1



1a-5a

1a X = Y = H
2a X = Y = OCH$_3$
3a X = Y = CF$_3$
4a X = Y = NO$_2$
5a X = OCH$_3$, Y = CF$_3$

6a-9a

6a X = Y = H
7a X = Y = OCH$_3$
8a X = Y = CF$_3$
9a X = OCH$_3$, Y = CF$_3$

1,1-diphenylethanol, that were assigned to the corresponding 1-oxaspiro[2,5]octadienyl radicals that formed after *O*-neophyl rearrangement of the triphenylmethoxyl and 1,1-dipenylethoxyl radicals.[3] However, Ingold reexamined these EPR data to provide, in both cases, an unambiguous reassignment from 1-oxaspiro[2,5]octadienyl radicals to phenoxyl radicals.[6]

Our own results that have been obtained recently for a series of symmetric and non-symmetric ring-substituted 1,1-diarylalkoxyl radicals, by means of product and time-resolved (LFP) kinetic studies, were instead interpreted in terms of a concerted mechanism.[7]

To obtain additional evidence on the concerted or stepwise nature of this rearrangement, we carried out hybrid DFT calculations of the potential energy surface (PES) relative to the reactions of the radicals **1a**−**6a** (see Chart 1). Although most of the experimental data are available for cyclopropyl-substituted radicals,[7] most of the calculations were carried out on the corresponding methyl-substituted ones. The substitution of methyl for cyclopropyl reduces the number of distinct conformational minima of the involved species but does not significantly affect the experimental and calculated rate constants (see below the results of **1a** vs **6a**).

The computed kinetic results here obtained have been compared with the experimental ones previously reported for **1a** and **6a**−**8a**[7] and with the additional experimental data, reported in Supporting Information, relative to the reaction of radical **9a**.

Results

Hybrid DFT calculations, at the UB3LYP/6-31G(d) level of theory, have been carried out for the reactions of the radicals **1a**−**6a** in the gas-phase. This level of theory was used because the results it provides for radicals have generally been found to be very reliable not only for equilibrium species but also for transition-states, as long as no sudden spin localization is required for the adiabatic passage from reactants to products.[8]

The geometry optimization of reactants, intermediates, and products, followed by location of the transition-states, has allowed for the calculation of all the stationary points of the potential energy curves. For the sake of illustration, the curve relative to the reaction of the radical **1a**, with reference to Scheme 2, is shown in Figure 1.

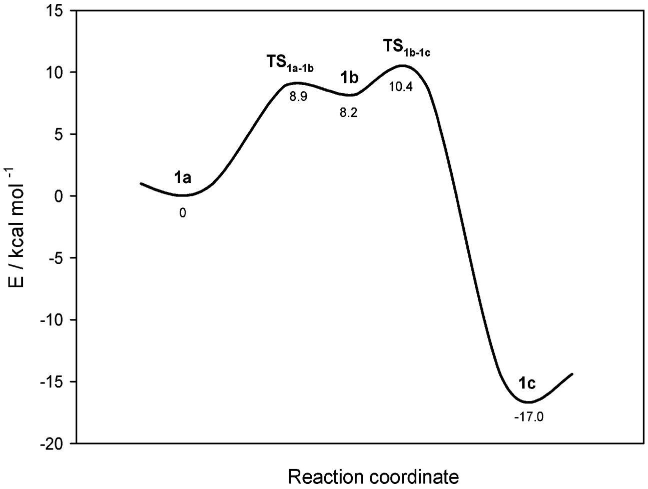


FIGURE 1. Gas-phase potential energy profile for the reaction of radical **1a** with reference to Scheme 2, calculated at the UB3LYP/6-31G(d) level of theory.

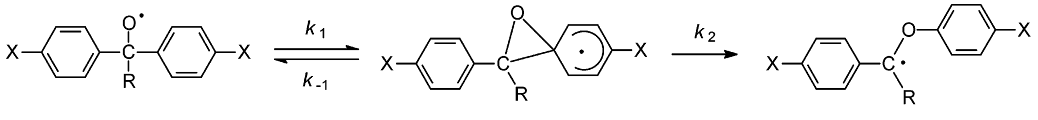
In the case of the unsymmetrically substituted radicals **5a** and **9a**, Scheme 3 holds.

The electronic energies, the electronic energies plus the corresponding zero-point vibrational energy (zpve) corrections, and the gas-phase free-energy differences ($\Delta G°$) for all the species are reported in Table 1 and take the corresponding reactant as a reference. When a given species exists as populations over multiple conformers (see Supporting Information), the data reported in Table 1 refer to the lowest-energy conformer. It has been verified that $\Delta G°$ values of the lowest-energy conformers and of the entire conformer populations differ by less than 0.1 kcal·mol^{-1}.

In all of the cases, with the possible exception of **5d**, the bridged 1-oxaspiro[2,5]octadienyl radical has been shown to be a minimum along the reaction coordinate, which corresponds to a short-lived intermediate. When an allowance is made for the zpve correction, the case of **5d** is ambiguous because its energy is practically coincident with that of the transition-state preceding its formation (TS$_{\mathbf{5a-5d}}$). This indicates the absence of any energy barrier that separates the low-energy vibrational levels of **5d** and TS$_{\mathbf{5a-5d}}$. Apart from this possible exception, the overall picture, at the temperature of 0 K appears to be quite consistent. The matter is not so clear-cut at 298 K, because a potential energy barrier less than rt (about 0.6 kcal·mol^{-1}) is negligible. From this point of view the existence of the bridged 1-oxaspiro[2,5]octadienyl radical as a distinct intermediate might be questionable in some of the cases reported in Table 1.

When focused on the overall energetics of the reaction series **1a**−**4a**, it is evident that the reaction depends on the energetic balance due to the cleavage of a C$_{Ar}$−C bond in the starting 1,1-diarylalkoxyl radical (**1a**−**4a**) and accompanied by the formation of a C$_{Ar}$−O bond in the rearranged carbon centered

SCHEME 2



1a-4a, 6a-8a **1b-4b, 6b-8b** **1c-4c, 6c-8c**

SCHEME 3

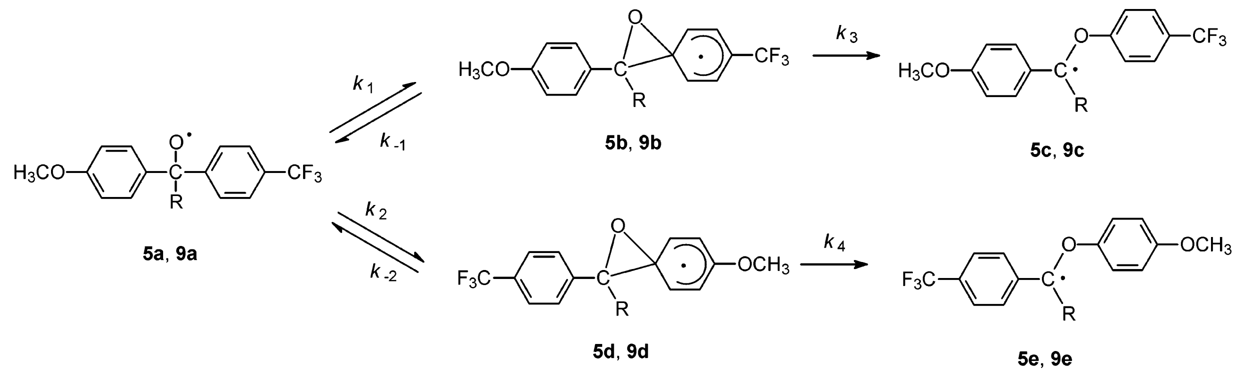


TABLE 1. Thermodynamic Data for the Reactions of the Radicals 1a−6a[a]

structure	electronic energy	electronic energy + zpve	Δ*G*° [b]
1a	0	0	0
TS$_{1a-1b}$	8.9	7.6	8.1
1b	8.2	7.2	7.4
TS$_{1b-1c}$	10.4	8.9	9.2
1c	−17.0	−17.4	−18.3
2a	0	0	0
TS$_{2a-2b}$	8.7	7.5	8.0
2b	8.4	7.4	7.6
TS$_{2b-2c}$	11.5	10.0	10.4
2c	−14.8	−15.4	−16.4
3a	0	0	0
TS$_{3a-3b}$	8.5	7.3	7.6
3b	7.1	6.3	6.5
TS$_{3b-3c}$	8.9	7.6	7.7
3c	−18.7	−19.0	−21.1
4a	0	0	0
TS$_{4a-4b}$	7.4	6.3	6.9
4b	4.9	4.2	4.6
TS$_{4b-4c}$	6.4	5.1	5.4
4c	−21.2	−21.3	−21.8
5a	0	0	0
TS$_{5a-5b}$	10.6	9.3	9.7
5b	9.2	8.2	8.0
TS$_{5b-5c}$	10.6	9.2	9.5
5c	−15.8	−16.3	−17.5
TS$_{5a-5d}$	9.1	7.8	8.3
5d	8.8	7.8	7.8
TS$_{5d-5e}$	11.7	10.2	10.5
5e	−15.3	−15.8	−17.3
6a	0.0	0.0	0.0
TS$_{6a-6b}$	8.9	7.7	8.2
6b	8.5	7.6	7.7
TS$_{6b-6c}$	10.6	9.2	9.5
6c	−17.2	−17.4	−18.3

[a] Reported in kcal·mol^{-1}. Calculated at the B3LYP/6-31G(d) level of theory relative to the corresponding reactant. [b] In the gas-phase at 298.15 K and 1 atm.

radical (**1c**−**4c**). Thus to properly discuss this balance, we have felt that it is also necessary to evaluate the gas-phase bond dissociation enthalpies (BDEs), at the same level of theory, for the cleavages of the two series of compounds, 4-XC_6H_4−CH_2OH and 4-XC_6H_4−OCH_3 (X = OCH_3, H, CF_3, NO_2), respectively, as described in Scheme 4.

SCHEME 4

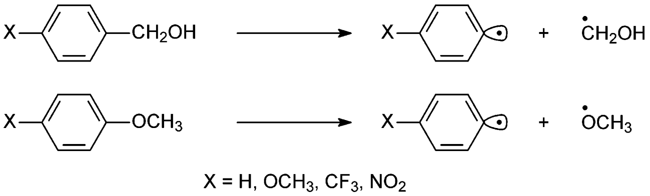


TABLE 2. Absolute and Relative Gas-Phase C_{Ar}−C and C_{Ar}−O BDEs of Para Substituted Benzyl Alcohols (4-XC_6H_4−CH_2OH) and Anisoles (4-XC_6H_4−OCH_3)[a]

X	4-XC_6H_4−CH_2OH	4-XC_6H_4−OCH_3
H	94.3 (0)	95.3 (0)
OCH_3	95.4 (+1.1)	94.8 (−0.5)
CF_3	94.8 (+0.5)	96.5 (+1.2)
NO_2	95.2 (+0.9)	97.7 (+2.4)

[a] Calculated at the UB3LYP/6-31G(d) level of theory, at 298.15 K, and at 1 atm. Reported in kcal·mol^{-1}. ΔBDEs values, in parentheses, are relative to X = H.

BDEs calculated at the UB3LYP/6-31G(d) level of theory are sufficiently reliable for the discussion presented here. It has been pointed out that the B3LYP functional offers an attractive and seemingly accurate alternative to the expensive conventional ab initio methods for the computation of BDEs[8] and that, thanks to the cancellation of errors, differences in BDEs (ΔBDEs) within a closely related family of compounds are much more reliable than the absolute values.[9] Absolute and relative BDEs thus obtained for C_{Ar}−C and C_{Ar}−O bond cleavage of ring-substituted benzyl alcohols and anisoles are collected in Table 2.

Discussion

Before getting to the heart of the discussion of the computational results, it is important to validate them by comparison against the available experimental data. Because most of the experimental data are available for cyclopropyl-substituted radicals,[7] whereas most of the calculations have been carried out, for practical convenience, on the corresponding methyl-substituted ones, the first question to resolve is the lack of a significant change of effects upon the substitution of methyl for cyclopropyl. It was already evidenced in a previous work that this substitution produces only a minor change in the observed rate constant of *O*-neophyl rearrangement on passing

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(5) 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.

(6) Ingold, K. U.; Smeu, M.; DiLabio, G. A. *J. Org. Chem.* **2006**, *71*, 9906−9908.

(7) Aureliano Antunes, C. S.; Bietti, M.; Ercolani, G.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 3884−3891.

(8) Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B. Eds.; Wiley-VCH: New York, 1999; Vol. 13, pp 1−97.

(9) Pratt, D. A.; DiLabio, G. A.; Mulder, P.; Ingold, K. U. *Acc. Chem. Res.* **2004**, *37*, 334−340 and references therein.

TABLE 3. Calculated Gas-Phase and Experimental Solution-Phase First-Order Rate Constants for the Rearrangement of Radicals 1a−9a

radical		k_{calc} s^{-1} [a]	k_{exp} s^{-1} [b]
1a	R = Me; X = Y = H	9.3×10^5	2.8×10^6 [c]
2a	R = Me; X = Y = OMe	1.5×10^5	
3a	R = Me; X = Y = CF_3	7.5×10^6	
4a	R = Me; X = Y = NO_2	5.3×10^7	
5a	R = Me; X = OMe, Y = CF_3	3.8×10^5 ($Q = 2.2$)	
6a	R = *c*-Pr; X = Y = H	5.9×10^5	2.0×10^6 [c]
7a	R = *c*-Pr; X = Y = OMe		2.6×10^5 [c]
8a	R = *c*-Pr; X = Y = CF_3		1.8×10^7 [c]
9a	R = *c*-Pr; X = OMe, Y = CF_3		5.1×10^5 [d] ($Q = 4.3$) [d,e]

[a] Gas-phase at 298.15 K and 1 atm. [b] MeCN solution at 295.15 K. [c] Ref 7. [d] This work (see Supporting Information). [e] Molar ratio of products obtained in CH_2Cl_2 at 293.15 K.

from radical **6a** to **1a** in a CH_3CN solution at 295.15 K (see Table 3).[7] Comparison between the $\Delta G°$ values for the reactions of radicals **1a** and **6a**, displayed in Table 1, shows that the data differ by ≤ 0.3 kcal·mol^{-1}. This is evidence that the substitution of methyl for cyclopropyl does not significantly affect the overall computational results. Validation of the computed data can therefore be realized, aside from the direct comparison with experimental data in the case of the radicals **1a** and **6a**, by comparing the computational data obtained for the methyl-substituted radicals **2a**, **3a**, and **5a** with the experimental data relative to the cyclopropyl-substituted ones **7a**−**9a**, respectively. To carry out such a comparison, the computed $\Delta G°$ values shown in Table 1 must be translated into rate constants. According to Hammett, in a consecutive reaction of the type shown in Scheme 2, it is only necessary for the free-energy of the intermediate (**b**) to be a couple of kilocalories or more higher than that of the reactant (**a**) for the Bodenstein steady-state approximation to apply.[10] This condition is largely verified for the cases at hand. Accordingly, the overall first-order rearrangement rate constants for the radicals that follow Scheme 2 will be given by eq 1.

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \tag{1}$$

One possible objection to the use of the steady-state approximation for all of the cases reported in Table 1 is that, at 298 K, in some of the examined cases, it is not absolutely clear if the 1-oxaspiro[2,5]octadienyl radical is actually an intermediate (see Results). However, we wish to point out that this objection is irrelevant because in these dubious cases $k_{-1} \gg k_2$ so that the overall rate constant is determined by the free-energy of the second transition-state, which is exactly the same result that one would obtain by considering a concerted reaction in which the first transition-state is ignored.

Analogously, for the case of an unsymmetrically substituted radical following Scheme 3, eqs 2 and 3 hold, where Q is the molar ratio **c**/**e** of the rearranged products.

$$k = \frac{k_1 k_3}{k_{-1} + k_3} + \frac{k_2 k_4}{k_{-2} + k_4} \tag{2}$$

$$Q = \frac{\dfrac{k_1 k_3}{k_{-1} + k_3}}{\dfrac{k_2 k_4}{k_{-2} + k_4}} \tag{3}$$

Microscopic rate constants appearing in eqs 1−3 have been calculated from the free-energies of activation reported in Table 1 by the canonical transition-state theory.[10,11] The gas-phase rate constants reported in Table 3 are calculated on the basis of either eq 1 or eq 2, and the available experimental rate constants are measured in a MeCN solution. In the case of unsymmetrically substituted radicals, the molar ratio Q is also reported.

Direct comparison between k_{exp} and k_{calc} for **1a** and **6a** shows that, in both cases, the experimental value is ≈3 times larger than the calculated one. Moreover, as indicated above, it is legitimate to compare k_{exp} for the cyclopropyl-substituted radicals **7a**−**9a** with k_{calc} relative to the corresponding methyl-substituted ones, **2a**, **3a**, and **5a**, respectively; the k_{exp} values are from 1.3 to 2.4 times larger than the k_{calc} ones. The conclusion is that the accordance between theoretically evaluated and experimental rate constants is extraordinarily good on the energy scale, which lends support to the reliability of the PESs evaluated at the UB3LYP/6-31G(d) level of theory. Further support comes from the comparison of the molar ratio Q in the case of the rearrangement of the unsymmetrically substituted radicals **5a** and **9a**; indeed the theory predicts that isomer **5c** is preferentially formed with respect to isomer **5e**, which is analogous to the experimentally observed predominance of isomer **9c** with respect to isomer **9e** (see Scheme 3 and Table 3).

The DFT computations thus provide strong support for the hypothesis that the *O*-neophyl rearrangement of 1,1-diarylalkoxyl radicals proceeds through the reversible formation of the reactive 1-oxaspiro[2,5]octadienyl radical intermediate. A reactive intermediate is typically present at very low, often undetectable, concentrations during the reaction course. In this sense, the above results are in contrast with the observations of Schuster[2] and Grossi,[3] which were successively challenged by Scaiano[4,5] and Ingold,[6] respectively, who suggested the accumulation of a relatively long-lived intermediate.

The above results are also in contrast to our own previous hypothesis of a concerted mechanism that appeared suitable to interpret the observed substituent electronic effects.[7] Indeed in our previous work we found excellent Hammett-type correlations between the σ^+ substituent constants and both the visible absorption band maxima of the reacting radicals and the rearrangement rate constants. These results were unduly interpreted as significant evidence of a reactant-like transition-state, and the latter was in contrast with a stepwise mechanism in which the formation of a high-energy intermediate is rate-determining.

The data in Table 1 provide a significant basis for the critical discussion of substituent effects on a consecutive reaction of the type $\mathbf{a} \leftrightarrows \mathbf{b} \rightarrow \mathbf{c}$. To this end we will focus on $\Delta G°$ values relative to the reactions of radicals **1a**−**4a**. The data relative to the 1-oxaspiro[2,5]octadienyl radical intermediates **1b**−**4b** show that the presence of methoxy ring substituents in **2b** determines a negligible effect with respect to the unsubstituted intermediate **1b** (7.6 vs 7.4 kcal·mol^{-1}), whereas a significant stabilizing effect is observed in the presence of electron-withdrawing substituents, which increases upon going from the CF_3-substituted radical **3b** (6.5 kcal·mol^{-1}) to the NO_2-substituted

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(10) Hammett, L. P. In *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970. Chapter 5.

(11) Cramer, C. J. *Essentials of Computational Chemistry − Theories and Models*, 2nd ed.; Wiley: Chichester, UK, 2004; pp 524−527.

one **4b** (4.6 kcal·mol^{-1}). A similar trend is observed, although, as expected, to a lesser degree, for the free-energies of the first transition-state TS_{a-b} relative to the formation of the bridged radical intermediate from the 1,1-diarylalkoxyl radical. In contrast, the second transition-state TS_{b-c}, relative to the transformation of the radical intermediate into the corresponding final carbon centered radical, appears to be much more sensitive to electronic effects, which spans about 5 kcal·mol^{-1} upon going from the OMe to the NO_2 group. Interestingly, this large sensitivity changes the relative importance of the two transition-states in affecting the observed reaction rate. Indeed, according to the steady-state approximation, the reaction rate is mostly affected by the transition-state which has the higher free-energy, no matter whether it is the first or the second transition-state.[10] The second transition-state, TS_{b-c}, has a higher free-energy than the first one, TS_{a-b}, in the cases of X = MeO and H and has comparable free-energy in the case of X = CF_3. Its free-energy decreases below the level of TS_{a-b} in the case of X = NO_2. The final carbon centered radical is also largely sensitive to electronic effects; its free-energy decreases by 5.4 kcal·mol^{-1} upon going from the OMe to the NO_2 group. The main contribution to the energetics of the process can be reasonably ascribed to the cleavage of a $C_{Ar}-C$ bond in the starting 1,1-diarylalkoxyl radical (**1a**−**4a**) that is accompanied by the formation of a $C_{Ar}-O$ bond in the rearranged carbon centered radical (**1c**−**4c**). Along this line, relative gas-phase $C_{Ar}-C$ and $C_{Ar}-O$ BDEs of para-substituted benzyl alcohols and anisoles, collected in Table 2, can help to shed light on the relative importance of the two processes. The data indeed show that, although all substituents determine a small but comparable increase in the $C_{Ar}-C$ BDE for the benzyl alcohol series, opposite effects are instead observed in the anisole series. The $C_{Ar}-O$ BDE slightly decreases in the presence of the OMe ring substituent and progressively increases upon going to the electron-withdrawing CF_3 and NO_2 substituents. Very importantly, the latter trend is analogous to that observed for the calculated reaction free-energy differences, $\Delta G°$, for the rearrangement of radicals **1a**−**4a** (Table 1) discussed above, which indicates that in the rearrangement the effect of ring substituents on the strength of the newly formed $C_{Ar}-O$ bond plays an important role. Along this line, the observations that the free-energy differences calculated for the bridged radical intermediate and the activation free-energies relative to its conversion into a carbon centered radical, $\Delta G°_{TSb-c}$, increase in the presence of electron-releasing substituents and decrease in the presence of electron-withdrawing ones (see above) can be interpreted similarly in terms of the substituent effect on the strength of the $C_{Ar}-O$ bond.

In conclusion, the results presented above show that DFT computational methods based on the hybrid B3LYP functional and on a basis set of moderate size such as 6-31G(d) can be conveniently used for the determination of kinetic data relative to neutral free-radical reactions. This is evidenced by the close adherence of the computational gas-phase rate constants to the experimental ones obtained in solution. The results point out to the reliability of the computed gas-phase mechanism of reaction. The bridged 1-oxaspiro[2,5]octadienyl radical has generally been shown to be a minimum along the reaction coordinate, which corresponds to a reactive intermediate. This is in contrast with previous hypotheses involving either a long-lived intermediate or the absence of this intermediate along the reaction path. The present study, moreover, indicates that, among the factors that govern the rearrangement, the strength of the $C_{Ar}-O$ bond that is formed during the rearrangement appears to play an important role.

Experimental Section

Computational Details. Hybrid DFT calculations have been carried out at the UB3LYP/6-31G(d) level of theory using the Gaussian 03 program package.[12] All species have been fully geometry optimized in the gas-phase and characterized as minima or transition-states by frequency calculations; the Cartesian coordinates are supplied in Supporting Information. The calculated spin-squared expectation values ($\langle S^2 \rangle$) were, after spin annihilation, ≤ 0.751 in all cases, which is in good agreement with the theoretically expected value of 0.75 for a pure doublet state. Transition-states have been located by the quadratic synchronous transit method (QST2). The eigenvector relative to the imaginary frequency of each transition-state has been carefully inspected with the help of the program GaussView[13] to check that it corresponded to the expected reaction coordinate. IRC calculations have been also carried out to confirm that the located transition-state actually connected the reactants and products from which it had been generated by the QST2 algorithm. Zero-point energies and gas-phase thermodynamic data at 298.15 K and 1 atm have been calculated by the standard harmonic approximation without any correction to vibrational frequencies.

Gas-phase BDEs at 298.15 K and 1 atm relative to the processes in Scheme 4, with X = OCH_3, H, CF_3, and NO_2, were also calculated by geometry optimization and frequency calculations of the involved species at the UB3LYP/6-31G(d) level of theory [BDE $= H^{\circ}_{298}(p\text{-}XC_6H_4^{\bullet}) + H^{\circ}_{298}(Y^{\bullet}) - H^{\circ}_{298}(p\text{-}XC_6H_4Y)$].

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Supporting Information Available: Results and experimental details of product and time-resolved studies for radical **9a**. Cartesian coordinates, potential energy, and thermodynamic data for all of the stationary points of the reaction of radicals **1a**−**6a** calculated at the UB3LYP/6-31G(d) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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