JOC Notes

Rearrangement of the 1,1-Diphenylethoxyl Radical Is Not Concerted but Occurs through a Bridged Intermediate

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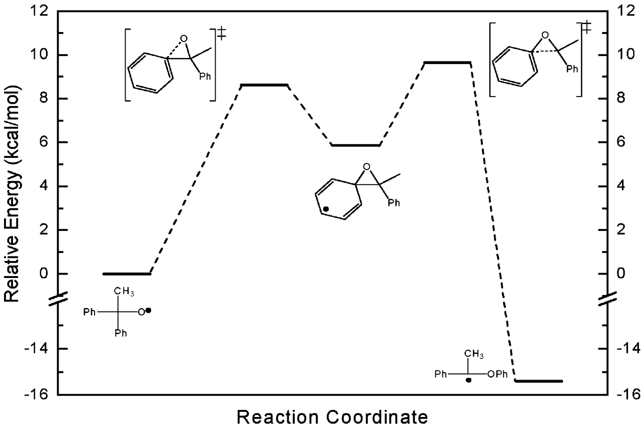
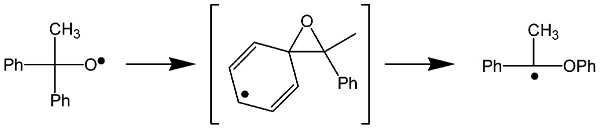


Recent experimental observations cast some doubt on the conclusions of earlier work that indicated that the rearrangement of 1,1-diphenylethoxyl radical occurs through a bridged intermediate. We show, by using carefully benchmarked DFT calculations, that the title rearrangement is indeed a two-step reaction.

Until recently, the mechanistic details of the neophyl-like rearrangement of the title radical (**I**) appeared to be fully elaborated. Clear evidence had been presented that showed that the rearrangement of the oxyl radical proceeds according to reaction 1 through a bridged intermediate to form the 1-phenoxy-1-phenylethyl radical (**III**). In one of the earliest works on this subject, Falvey et al.[1] observed in 1990 that the photolysis of *t*-butyl-1,1-diphenylethyl peroxide resulted in two intermediates with absorbance maxima at 535 nm and at 400 nm.[2] On the basis that the absorbance maximum of the spiro[2,5]octadienyl radical occurs at 560 nm,[3] Falvey et al. proposed that the peak at 535 nm was due to **II** and that the shorter wavelength peak was due to the longer-lived **III**.



I **II** **III** (1)

Banks and Scaiano[4] later re-examined reaction 1 by means of laser flash and laser drop photolysis. They also observed an absorption at $\lambda_{max} = 535$ nm for which the decay kinetics were consistent with the appearance kinetics of a peak at 320 nm. Contrary to Falvey et al., Banks and Scaiano assigned the band at 535 nm to **I** and not to the bridged intermediate **II**, and they indicated that the band at 320 nm is due to the carbon-centered radical **III**. Their rate data indicate that reaction 1 has an activation energy of 5.9 ± 0.4 kcal/mol and suggest that an intermediate (**II**) may have been involved in the reaction but was too short-lived to be observed using their techniques. The results of their low-level, semiempirical quantum mechanical simulations provided qualitative support for their experimental findings.

In 2000, Grossi and Strazzari[5] presented seemingly convincing evidence that reaction 1 is indeed a stepwise reaction. Using electron spin resonance (ESR) spectroscopy, they claimed to have measured hyperfine splitting constants of the never before observed rearrangement intermediate (**II**). However, we became certain that their assignment was incorrect after careful examination of the *g* values, which were much too high to be from **II**.[6]

The case established for reaction 1 to occur as a two-step reaction was put into doubt by a recent product and time-resolved kinetic study by Aureliano Antunes et al.[7] The authors of that work expressed some doubt over the findings presented in previous studies[1,4,5] and uncertainty over the semiempirical quantum mechanical results obtained by Banks and Scaiano.[4] On the basis that the rearrangement of reaction 1 is controlled by electronic effects in **I** that result in transition-state structures (TS) with reactant-like character, Aureliano Antunes et al. hypothesized that reaction 1 occurs via a concerted process. A subsequent work[8] supports some of the findings in ref 7 with respect to solvent effects on rearrangement rates, but it did not help to distinguish between the concerted or stepwise reaction mechanism for reaction 1.

In this note we aim to shed some light on the rearrangement of the 1,1-diphenylethoxyl radical with the use of computational chemistry. The calculation methods and computing power that were available to Banks and Scaiano at the time of their study were limited. However, we now have the ability to treat these

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

(2) The rapid rearrangement in **1** prevents β scission.

(3) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063−6068.

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

(5) Grossi, L.; Strazzari, S. *J. Org. Chem.* **2000**, *65*, 2748−2754.

(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) Bietti, M.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 10603−10606.

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TABLE 1. Energies of the Selected[a] Excitations of the Reactant[b]

radical	excitation energy (nm)	oscillator strength $\times 10^3$
1,1-diphenylethoxyl, **I**	628	12.6
	531	4.2
	501	3.0
	463	36.9
	316	1.1
	310	3.8
1-oxaspiro[2,5]octadienyl, **II**	370	32.4
	357	8.1
	337	7.8
	331	33.7
	324	1.3
	317	8.4
	306	56.1
1-phenoxy-1-phenylethyl radical, **III**	401	2.4
	369	1.6
	347	100.2
	324	23.9
	323	8.4

[a] Excitations from 300 to 700 nm with oscillator strengths greater than 0.001 are listed. A complete listing of the 12 calculated excitation energies for each radical is given in the Supporting Information. [b] Bridged and product radicals in reaction 1 were calculated by B3LYP[15,16]/6-311+G(d,p).

systems with reasonably high levels of theory. Nevertheless, the large size of the radicals prevents us from applying very accurate, highly correlated wavefunction methods with large basis sets. Instead, we use carefully benchmarked DFT techniques to investigate the energetics associated with reaction 1.[9−12]

We begin by presenting some calculated properties for the radicals in reaction 1 to make comparisons to those measured in previous experiments. Table 1 contains selected time-dependent DFT excitation energies (all computed data are given in Table S1 of Supporting Information). There are several calculated excitations that appear in the 300−700 nm window. Our results agree with those of Banks and Scaiano in that only the alkoxyl radical **I** has a peak near 535 nm (calculated at 531 nm). The most intense calculated peak for **I** appears at 463 nm, which coincides with an unassigned λ in Figure 1 of ref 4. We note that, according to our previous experience,[14] oscillator strengths that are associated with electronic excitations in radicals tend to be poorly predicted when using the applied technique. The same is true in the present case: The calculated 531/463 peak ratio of 0.11 does not match the ca. 1.4 ratio measured in ref 4. Nevertheless, the agreement in excitation energies is quite good.

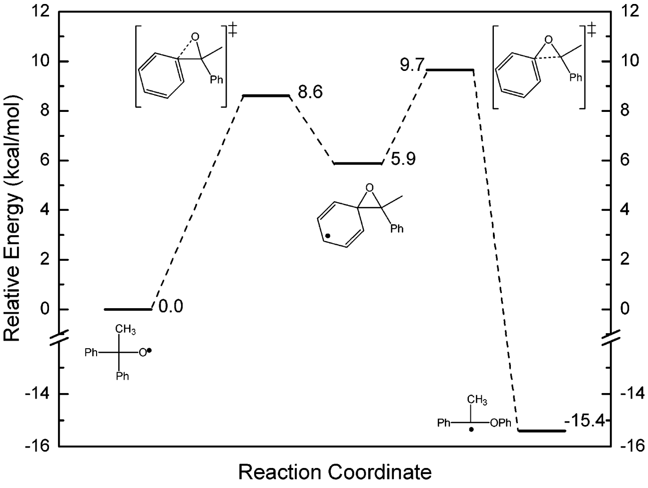

FIGURE 1. Relative energy diagram for reaction 1. Values are zero-point energy corrected and are shown on the diagram next to the energy levels.

Both **II** and **III** have substantial delocalized electron character in their phenyl rings, and so we are not surprised that both radicals have similar calculated excitations in the 300−400 nm range. Our calculations predict that both species can account for the grow-in peak at 325 nm that was observed by Banks and Scaiano. It is possible that the spectra near 325 nm as obtained in ref 4 represent, to some extent, a convolution of absorbances due to **II** and **III** if the intermediate is long-lived enough.

Overall, the results of our excited-state calculations are very consistent with the experimental findings presented in ref 1 and 4. The calculations support the peak assignments made by Banks and Scaiano.

The calculated energetics associated with reaction 1 are shown in Figure 1. Our results indicate that there is indeed a bridged intermediate in the reaction and that it lies 5.9 kcal/mol above the alkoxyl radical. **I** and **II** are separated by a barrier of 8.6 kcal/mol (E_a = 9.1 kcal/mol) in the "forward" direction. The intermediate is separated from the energetically low-lying phenylethyl radical by a barrier of ca. 3.8 kcal/mol. The data shown in Figure 1 are corrected for zero-point energies. Thus, the minimum associated with **II** is a "real" minimum, which supports at least one vibrational level. The reaction profile is close to but not completely symmetric about **II**, and the rate-limiting step is the first step in the reaction. Our computed E_a

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(9) All calculations we performed with Gaussian Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Wallingford, CT, 2004.

(10) The MPW1K/6−31+G(d,p) method was selected for geometry optimizations and energy evaluations following extensive benchmarking efforts that are provided in Supporting Information. We summarize those data by stating that the MPW1K[11] results are in good agreement with those based on cc-pVDZ-TZ extrapolated CCSD(T) energies for reduced models of the systems under investigation.

(11) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811−4815.

(12) We used the MPW1k approach to compute the thermochemistry and kinetics associated with the neophyl rearrangement. Our calculated data, $E_a = 13.0$ kcal/mol, $\log(A/\mathrm{s}^{-1}) = 13.4$, and $\log(k(298\ \mathrm{k})/\mathrm{s}^{-1}) = 4.2$, are in excellent agreement with the most recently reported experimental results on this topic, $\log(k/\mathrm{s}^{-1}) = (12.7 \pm 0.3) - [(13.8 \pm 0.4)/(2.303RT)]$, which were obtained by Weber and Fischer.[13]

(13) Weber, M.; Fischer, H. *J. Am. Chem. Soc.* **1999**, *121*, 7381−7388.

(14) DiLabio, G. A.; Litwinieko, G.; Lin, S.; Pratt, D. A.; Ingold, K. U. *J. Phys. Chem. A* **2002**, *106*, 11719−11725.

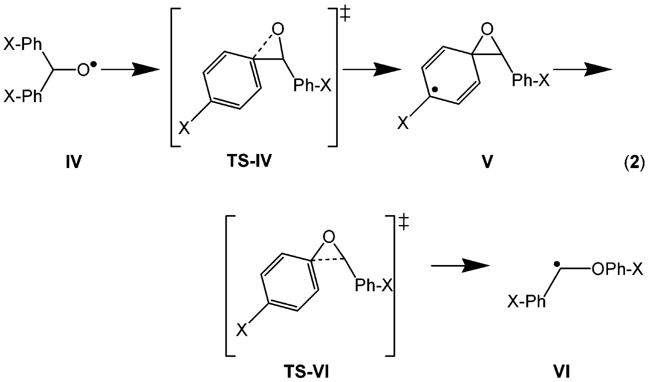
(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5642.

(16) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

is 2.8 kcal/mol higher than the upper bound on the value reported by Banks and Scaiano.

Our calculations indicate that the TS structure associated with the rate-determining (i.e., first) step of **1** has reactant-like character. This supports the observations of Aureliano Antunes et al.[7] The shallow minimum associated with the intermediate explains why it has been difficult to observe.

We performed additional calculations to characterize the effects of para ring substitutents on the *O*-neophyl rearrangement. For this work, we replaced the methyl group at the tertiary carbon center with a hydrogen atom; see reaction **2**. The data compiled in Supporting Information gives us confidence that this substitution has small effects on the predicted properties and the relative energies.



(**2**)

In Table 2, we show the relative energies for reaction 2 with a series of electron-donating (ED) and electron-withdrawing (EW) substitutents along with the calculated gas-phase first-order rate constants. The analysis of those data indicates that all substituents have a slight lowering effect on **TS-IV** that is irregular with the strength of the ED or the EW group. We understand this result in terms of simple substitutent effects in para-substituted toluenes.[17,18] The **TS-IV** structures are reactant-like and resemble 4-X$-C_6H_4-CH_3$ molecules on which ED and EW Xs have small effects. For example, the changes in the molecular stabilization enthalpy[19] in 4-X$-C_6H_4-CH_3$ relative to X = H range from 0 to 0.8 kcal/mol.[17] The relative energies of the intermediate structures **V** are only slightly affected by ED groups but are strongly stabilized by most EW groups. The large stabilizations are the result of EW through the σ-frame and by π-delocalization of the unpaired electron into the available empty p- or π-type orbitals that are available in the substituents. Because there are structural similarities between **TS-VI** and **VI**, substituent effects on their relative energies are also similar. In these cases, the substituent effects are due to the convolution of radical stabilization enthalpies (RSE) on the benzyl moieties and also to the molecule stabilization enthalpies (MSE) on the phenoxy moieties of the **TS-VI** and **VI** species (see Table 5 of ref 17 for MSE and RSE values).

TABLE 2. Relative Energies[a] with Various para-X-Substituents and Gas-Phase, First-Order Rate Constants[b] for Reaction 2[c]

X	TS-IV	V	TS-VI	VI	log *k*
$N(CH_3)_2$	−0.9	0.2	1.7	2.9	4.3[d]
NH_2	−1.0	−0.2	1.3	2.7	4.7
OCH_3	−0.2	0.3	1.2	2.2	4.7
OH	−0.2	0.4	1.2	2.1	4.7
CH_3	−0.3	−0.2	0.2	0.7	5.2
H	0 (9.9)	0 (7.3)	0 (10.7)	0 (−13.7)	5.4[e]
COOH	−0.7	−2.1	−2.5	−2.5	6.6
CHO	−1.2	−3.0	−3.2	−3.0	6.9
CF_3	0.0	−0.6	−1.0	−1.4	5.8
CN	−1.0	−2.6	−2.6	−2.5	6.8
NO_2	−0.5	−2.3	−2.9	−3.2	6.5[f]

[a] Zero-point energy corrected values are reported in kcal/mol. [b] The value of *k* is in units of s^{-1}. Energy entries are relative to the X = H values.[c] The data in brackets are energies for X = H relative to **IV**. [d-f] The presence of a methyl group at the central, tertiary carbon raises log *k* to [d]5.5, [e]6.9, [f]7.7, see Supporting Information. Our calculated value for log *k* for reaction **2** with X = H and a methyl group on the central carbon is in excellent agreement with the measured value of 6.45 reported in ref 7.

Table 2 also shows the effect of the substituent group on the rate constant (*k*) for reaction 2, which was calculated using a steady-state approximation that involves a pre-equilibrium as described by Atkins.[20,21] The value of *k* is lowest for the strongest ED groups, and it increases with increasing EW strength of the substituent. There is a difference of 2 orders of magnitude in *k* over the range of substitutents studied.

Overall, the calculated substituent effects on the rate constants are in line with the observations of Aureliano Antunes et al.[7] who reported that "migration aptitudes" displayed the following trend with X: $CF_3 > H \cong CH_3 > OCH_3$. The data in Table 2 indicate that the migratory aptitudes arise from the substituent effects on the relative stabilities on the intermediate and second barrier in reaction 2: That is, the destabilization of **V** and **TS-VI** follow the order $CF_3 > H \cong CH_3 > OCH_3$.

Consideration of how the substituents change the barrier heights in reaction 2 with respect to **V** can give us some idea of how structure can influence the lifetime (and hence the ease of observation) of the reaction intermediate. In this context, the differences in relative energies between **TS-IV** and **V** (Table 2, columns 2 and 3) and also between **TS-VI** and **V** (Table 2, columns 3 and 4) indicate that aryl substituents have the potential to contribute less than 2 kcal/mol to stabilizing **V** with respect to its barriers. The largest overall effect on the intermediate lifetime is likely to come from −CN substituents, which lowers **V** by 1.6 kcal/mol with respect to **TS-IV** but causes no change in the **V**−**TS-VI** separation. The use of CF_3 substituents by Aureliano Antunes et al. was only moderately effective in this connection, which lowered **V** by 0.6 kcal/mol with respect to **TS-IV** but also lowered **TS-VI** by 0.4 kcal/mol with respect to **V**.

In summary, the results of our theoretical calculations predict properties that are associated with the radicals in the 1,1-diphenylethoxyl radical rearrangement of **1** that reproduce those obtained from experiment. The rate constants we calculated are

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(17) Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 11085−11092.

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

(19) The molecular stabilization enthalpy for para-substituted toluene is derived from the reaction 4-X$-C_6H_4CH_3 + C_6H_6 \rightarrow C_6H_5X + C_6H_5CH_3$. Similarly, a radical stabilization enthalpy can be obtained from 4-X$-C_6H_4$-$CH_2^\bullet + C_6H_6 \rightarrow C_6H_5X + C_6H_5CH_3^\bullet$. See refs 17 and 18 for details.

(20) Atkins, P. W. *Physical Chemistry*, 6th ed.; W. H. Freeman and Company: New York, 2000; Chapter 25.

(21) The rate constants for the reactions were evaluated according to $k = k_I k_{II}/k_{-I} + k_{II}$. For example, the rate constants for reaction **1** are those associated with the process I → II (k_I), II → I (k_{-I}), and II → III (k_{II}). For a given process, rate constants were calculated using $k = A_q e^{-\Delta E°/RT}$ with $A_q = (kT/h)(Q^‡/Q^R)$ where *R* is the gas constant, *T* is the temperature (298.15 K), *k* is the Boltzmann constant, *h* is Planck's constant and $Q^‡$ and Q^R are the partition functions for the states in their lowest vibrational level. $\Delta E°$ includes the zero-point energy difference between the reactant and transition state.

in agreement with the trend observed experimentally.[7] Relative energies obtained from a carefully benchmarked DFT approach show that reaction 1 indeed proceeds through an intermediate.

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Supporting Information Available: Calculated data including excitation energies and oscillator strengths for **I**−**VI**, energies and rate constants for **S1** and **2**, benchmark data for **2** from several computational methods, optimized Cartesian coordinates for the species in **1**, **2**, and **S1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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