JOC*Note*

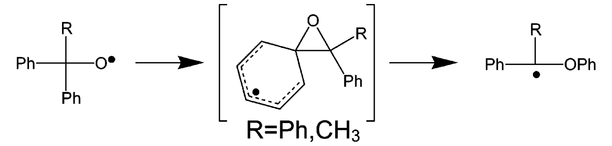
Isomerization of Triphenylmethoxyl and 1,1-Diphenylethoxyl Radicals. Revised Assignment of the Electron-Spin Resonance Spectra of Purported Intermediates Formed during the Ceric Ammonium Nitrate Mediated Photooxidation of Aryl Carbinols

K. U. Ingold,*,† Manuel Smeu,‡,§ and Gino A. DiLabio§

National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6, Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2E1, and National Institute for Nanotechnology, National Research Council of Canada, 11421 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2M9

keith.ingold@nrc.ca

Received September 13, 2006



Grossi and Strazzari have reported (*J. Org. Chem*. **2000**, *65*, 2748−2754) that the ceric ammonium nitrate modulated photooxidation of triphenylmethanol and 1,1-diphenylethanol yielded ESR spectra of the putative spiro-cyclohexadienyl intermediates in the *O*-neophyl rearrangements of the corresponding alkoxyl radicals, $Ph_2(R)CO^\bullet$ (R = Ph, CH_3), to the phenoxymethyl radicals, $Ph(R)C^\bullet OPh$. Both ESR spectra are reassigned to the phenoxyl radical, $C_6H_5O^\bullet$, and the probable mechanism by which phenoxyl is formed in these systems is presented.

Almost a century ago, Wieland[1] reported the first free-radical rearrangement. He discovered that the thermal decomposition of bis(triphenylmethyl) peroxide yielded 60−70% of 1,2-diphenoxy-1,1,2,2-tetraphenylethane, reaction 1, and interpreted this result in terms of an initial formation of triphenylmethoxyl radicals, reaction 2, and their isomerization to diphenylphenoxymethyl followed by coupling of two of these carbon-centered radicals, reactions 3 and 4.

$$Ph_3COOCPh_3 \rightarrow Ph_2C(OPh)C(OPh)Ph_2 \tag{1}$$

$$Ph_3COOCPh_3 \rightarrow 2Ph_3CO^\bullet \tag{2}$$

$$Ph_3CO^\bullet \rightarrow Ph_2C^\bullet OPh \tag{3}$$

$$2Ph_2C^\bullet OPh \rightarrow Ph_2C(OPh)C(OPh)Ph_2 \tag{4}$$

Roughly half a century later, one of us reported[2] that the 1,1-diphenylethoxyl radical, generated at 30 °C by various procedures, underwent an analogous 1,2-phenyl group migration, reaction 5.

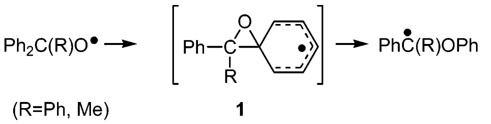
$$Ph_2C(Me)O^\bullet \rightarrow PhC^\bullet(Me)OPh \tag{5}$$

This isomerization was much faster than the anticipated β-scission, reaction 6,

$$Ph_2C(Me)O^\bullet \rightarrow Ph_2CO + Me^\bullet \tag{6}$$

a result that was later used[3] to estimate that the rate constant for reaction 5, k_5, must be greater than 10^6 s^{-1}.

Reactions 3 and 5 must proceed through a spiro-cyclohexadienyl radical, **1**. A hotly debated question has been whether **1**, for R = Ph and Me, is a discrete intermediate or is simply a representation of the transition state for a concerted phenyl group migration.[4] Schuster and co-workers[7] pioneered the use of picosecond laser flash photolysis (LFP) to address this question for both radical isomerizations. LFP of $Ph_3COOCMe_3$ in acetonitrile at room temperature was found to yield a transient absorbance (λ_{max} = 545 nm) "instantaneously", i.e., within the rise time of the laser pulse (17 ps) that persisted for several hundred microseconds. This absorbance was assigned to the $Ph_2C^\bullet OPh$ radical by analogy with the known spectrum of the structurally related $Ph_2C^\bullet OH$ radical, and k_3 was estimated to be $>5 \times 10^{10}$ s^{-1}.[8] LFP of $Ph_2C(Me)OOCMe_3$ under the same conditions "instantaneously" gave a transient absorbance (λ_{max} = 535 nm) that decayed with first-order kinetics and, in the



1 (7)

---

† National Research Council of Canada.

‡ University of Alberta.

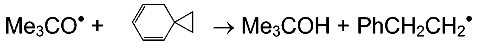
§ National Institute for Nanotechnology.

(1) Wieland, H. *Chem. Ber.* **1911**, *44*, 2550−2556.

(2) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3797−3801. See also: Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3793−3795.

(3) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 2.

(4) No intermediate cyclohexadienyl radical has been observed in any analogous arylmethyl radical isomerizations, i.e., in the neophyl, $PhC(Me)_2CH_2^\bullet \rightarrow PhCH_2C^\bullet Me_2$, and similar rearrangements.[5] Indeed, the reaction of spiro[2.5]octa-4,6-diene with photogenerated *tert*-butoxyl radicals at −166 °C in propane in an ESR spectrometer gave only the spectrum of the 2-phenylethyl radical:[6]



This is not, however, a concerted reaction because a cyclohexadienyl radical was detected by its absorption and fluorescence when this reaction was carried out at room temperature using nanosecond laser flash photolysis.[6]

(5) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 4.

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

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

10.1021/jo061898z CCC: $33.50 © 2006 American Chemical Society
Published on Web 12/01/2006

absence of good hydrogen atom donors, gave rise to a second species ($\lambda_{max} = 410$ nm) that also persisted for several hundred microseconds. This second transient absorption was assigned to the $PhC^{\bullet}(Me)OPh$ radical by analogy with the known spectrum of the $PhC^{\bullet}(Me)OH$ radical.[7] The first transient ($\lambda_{max} = 535$ nm) was quenched, i.e., decayed more rapidly following (pseudo)-first-order kinetics, by the fairly good H-atom donor, 1,3-dioxolane. In the absence of H-atom donors, decay occurred with a rate constant of 3.2×10^6 s^{-1}. This first transient was assigned to the cyclohexadienyl intermediate, **1** (R = Me), that had to be assumed to be in equilibrium with its precursor alkoxyl radical to account for the above-mentioned quenching. This assignment was made by analogy with an all-carbon analogue of **1**[4,6] and because "no known alkoxy(l) radicals possess absorptions in the visible region of the spectrum."[7] However, it was later found that $ArC(R,R')O^{\bullet}$ radicals as a class absorb in the 530−590 nm region.[9]

The unequivocal identification of Schuster's 535 nm transient as the $Ph_2C(Me)O^{\bullet}$ radical is due to Banks and Scaiano,[10] who used nanosecond LFP with the same precursor, $Ph_2C(Me)OOCMe_3$. In acetonitrile at 22 °C, these workers obtained $k_5 = 2.5 \times 10^6$ s^{-1}, in good agreement with Schuster's rate constant (3.2×10^6 s^{-1})[7] and with the earlier estimate ($>10^6$ s^{-1}).[2,3] Subsequently, Bietti and co-workers obtained $k_5 = 2.8 \times 10^6$ s^{-1} in acetonitrile at 22 °C and showed that rate constants were influenced to a small extent by ring substituents[11] and solvent.[12]

The kinetic picture painted by LFP for the isomerization of $Ph_3CO^{\bullet}$ and $Ph_2C(Me)O^{\bullet}$ are internally consistent and indicate that conversion to the corresponding carbon-centered radicals are very fast with no intermediate, **1**, being detectable. The only electron spin resonance (ESR) study of these two reactions caused conclusions to be drawn that stand in stark contrast to the conclusions drawn from the LFP work. In 2000, Grossi and Strazzari[14] reported ESR spectra obtained during the photooxidation by ceric ammonium nitrate (CAN) of triphenylmethanol and 1,1-diphenylethanol in acetonitrile at 230 K that were very similar. Both radicals had hyperfine splittings (hfs) produced by five hydrogen atoms: a single H, and two pairs of equivalent H's, and had g values of 2.0053.[14] These hfs were attributed to the five hydrogen atoms on the cyclohexadienyl ring moiety of **1**. Their magnitudes (in mT) and assignments were as follows: for the Ph_3COH system, $a(H_4) = 1.008$, $a(H_3,H_5) = 0.19$, $a(H_2,H_6) = 0.671$; and for the $Ph_2C(Me)OH$ system, $a(H_4) = 1.005$, $a(H_3,H_5) = 0.195$, $a(H_2,H_6) = 0.675$.[15] The spectrum obtained from $Ph_2C(CD_3)OH$ was the same as that from $Ph_2C(Me)OH$, while that from $(C_6D_5)_2C(Me)OH$ was characterized by deuterium hfs each of ca. 1/6.5 those of the corresponding protons in the spectra from $Ph_2C(Me)OH$ and $Ph_2C(CD_3)OH$. There can therefore be no doubt that the observed ESR spectra[16] arise from the interaction of the unpaired electron with one of the phenyl rings from the starting alcohol.

Grossi and Strazzari[14] were aware of the earlier LFP work[7,10] where there was no sign of the **1** intermediates to which they assigned their ESR spectra. The ESR time scale is milliseconds to microseconds, and ESR is, therefore, much less capable of detecting very short-lived intermediates than are nano- and picosecond LFP. Moreover, Grossi and Strazzari failed to detect **1** (R = Me) when $Ph_2C(Me)OOC(Me)Ph_2$ was photolyzed in acetonitrile at 230 K in the ESR cavity. These workers were therefore forced to propose that "an important role is played by CAN in the formation and in the stabilization of this intermediate" (i.e., **1**). They went on to suggest that **1** was stabilized inside the coordination sphere of the cerium ion. This would be an unprecedented stabilization of a radical against a unimolecular ring-opening rearrangement. Surprisingly, although this paper[14] has been cited roughly a dozen times it has received only one mildly critical comment, viz., Grossi and Strazzari's report "raises some doubt on the involvement of free alkoxyl radicals in the CAN-induced photooxidation of arylcarbinols".[11]

The contrast between the conclusions drawn from LFP and ESR studies of these *O*-neophyl rearrangements induced us to re-examine the published work. We quickly focused on Grossi and Strazzari's assignments of their ESR spectra to the cyclohexadienyl radicals, **1** (R = Ph, Me). The relevant hydrogen hfs (mT) for the parent cyclohexadienyl radical, $C_6H_7^{\bullet}$, are:[17] $a(H_4) \sim 1.3$, $a(H_3,H_5) \sim 0.27$, and $a(H_2,H_6) \sim 0.9$. These values are only roughly similar to those reported[14] for **1** (R = Ph and Me), see above, and they change little upon ring substitution by nonconjugating substituents.[17] Thus, the hfs by themselves should be enough to raise doubts about the ESR spectra attributed[14] to **1** actually arising from such radicals. Certainty that this assignment is incorrect comes from an examination of *g* values. All cyclohexadienyl radicals having only hydrogen, deuterium, carbon, or oxygen atom attached to the 6-membered ring's carbon atoms and for which *g* values have been reported (ca. 78 species)[17] have *g* values in the range 2.00223−2.0039 (mean 2.00293). Radicals with the much higher *g* values of 2.0053 simply cannot be cyclohexadienyls, and therefore, their assignment to **1** (R = Ph and Me) is incorrect. Fortunately, their high *g* values indicate that the unpaired electron resides largely on one (or more) heteroatoms, not mainly on carbon atoms. With this clue, it is straightforward to identify *both* radicals purported to have structure **1** as phenoxyl, $C_6H_5O^{\bullet}$, for which[18] $g = 2.0053$, $a(H_4) = 1.0013$, $a(H_3,H_5) = 0.205$, $a(H_2,H_6) = 0.701$.[15,19]

There are several possible mechanisms by which the phenoxyl radical might be produced during the CAN-mediated photooxidation of the two aryl carbinols, not all of which involve an intermediate alkoxyl radical. However, the fact that the CAN-

---

[8] This rate constant may be an overestimate because the precursor radical, $Ph_3CO^{\bullet}$, would be expected to have an absorption at about the same wavelength (see refs 9−12 and text). This would make $Ph_3CO^{\bullet}$ difficult to identify as a precursor of the $Ph_2C^{\bullet}OPh$ radical. Nevertheless, the isomerization of $Ph_3CO^{\bullet}$ must be very fast because the photolysis of $Ph_3COOCMe_3$ in neat isopropanol (13.0 M) yielded <0.5% Ph_3COH.[7] The rate constant for the reaction: $Me_3CO^{\bullet} + Me_2CHOH \rightarrow Me_3COH + Me_2C^{\bullet}OH$, is 1.8×10^6 s^{-1},[13] and assuming a similar rate constant for the $Ph_3CO^{\bullet}$ reaction, the < 0.5 % yield of Ph_3COH translates to $k_3 > 5 \times 10^9$ M^{-1} s^{-1}.

[9] Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576−6577. See also: Avila, D. V.; Ingold, K. U.; Di Nada, A. A.; Zerbetto, F.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 2711−2718.

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

[11] Antunes, C. A. A.; Bietti, M.; Ercolani, G.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 3884−3891.

[12] Bietti, M.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 10603−10606.

[13] Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520−4527.

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

[15] Note that differences in hfs < ~0.03 mT do not necessarily indicate that the ESR spectra arise from different radicals when the signal-to-noise ratios are poor (as was the case for the radicals reported in ref 14).

[16] The acetonitrile solvent was purged with nitrogen but the solutions were not completely free of oxygen because the ESR signals due to peroxyl radicals (single broad line, $g = 2.015$) were also present.[14]

[17] Berndt, A. In *Landolt-Börnstein, New Series: Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, 1977; Vol. 9b, pp 452−492; 1987; Vol. 17c, pp 88−105.

[18] Graf, F.; Loth, K.; Günthard, H. H. *Helv. Chim. Acta* **1977**, *60*, 710−721.

mediated photooxidation of cumyl alcohol in acetonitrile yielded ESR spectra of the methyl radical and the NCCH2$^\bullet$ radical[14,22] provides strong evidence that PhC(R,R′)O$^\bullet$ radicals are, indeed, formed from PhC(R,R′)OH in these systems. That is, phenyl migration to oxygen has never been observed in cumyloxyl radical chemistry. Instead, this radical undergoes β-scission and/or H-atom abstraction from the solvent, reactions 8 and 9.

$$\mathrm{PhCMe_2O^\bullet \rightarrow PhCOMe + Me^\bullet} \tag{8}$$

$$\mathrm{PhCMe_2O^\bullet + CH_3CN \rightarrow PhCMe_2OH + {}^\bullet CH_2CN} \tag{9}$$

The mechanism by which alkoxyl radicals are formed in these systems has not been elucidated, although it has been suggested[23] that aryl carbinol/Ce(IV) 1:1 complexes[24] are involved. Grossi and Stazzari,[14] employing a 3-fold excess of alcohol (20 mM) over CAN (0.5 wt %, 7 mM), proposed that **1** were formed by an electron transfer from the alcoholic oxygen atom to the photoexcited, complexed cerium ion. Since **1** were not actually detected, an alternative[23] is that alkoxyl radicals are formed by direct photolysis of the Ce–O bond, e.g., reaction 10.

$$\mathrm{PhCMe_2OH + Ce(IV) \rightleftharpoons H^+ + PhCMe_2OCe(III) \xrightarrow{h\nu} PhCMe_2O^\bullet + Ce(III)} \tag{10}$$

A one-electron oxidation of the alcohol by the nitrate radical, NO$_3^\bullet$ (known to be produced upon photolysis of CAN),[25] is unlikely to yield the radical cation of the alcohol.[23,26] However, it might yield the alkoxyl radical by a hydrogen atom transfer (HAT) or proton-coupled electron-transfer (PCET) mechanism, e.g.

$$\mathrm{PhCMe_2OH + NO_3^\bullet \rightarrow PhCMe_2O^\bullet + HNO_3 \rightleftharpoons H^+ + NO_3^-} \tag{11}$$

At all events, for those alkoxyl radicals that undergo fast phenyl group migration to oxygen, reaction 7, some fraction of the resulting carbon-centered radicals are directly oxidized to a carbocation by the 7 mM ceric ion present in the acetonitrile, reaction 12,

$$\mathrm{PhC^\bullet(R)OPh + Ce^{IV} \rightarrow PhC^+(R)OPh + Ce^{III}} \tag{12}$$

while most, or all, of the remainder are trapped by residual dioxygen to form the peroxyl radicals observed in these systems,[14,16,30] reaction 13.

$$\mathrm{PhC^\bullet(R)OPh + O_2 \rightarrow PhC(OO^\bullet)(R)OPh} \tag{13}$$

The acetonitrile was HPLC grade and would have contained sufficient water to trap some or all of the carbocations, reaction 14,

$$\mathrm{PhC^+(R)OPh + H_2O \rightarrow H^+ + [PhC(R)(OH)OPh] \rightarrow PhCOR + PhOH} \tag{14}$$

and the phenol released in this process would have been oxidized to phenoxyl by ceric ion, reaction 15, a process that is known to be fast even in the absence of UV irradiation.[21,31]

$$\mathrm{PhOH + Ce^{IV} \rightarrow PhO^\bullet + Ce^{III}} \tag{15}$$

In conclusion, there is no unequivocal experimental evidence that the spiro-cyclohexadienyl radicals, **1** (R = Ph and Me), are, or are not, genuine intermediates in these two *O*-neophyl rearrangements. These are questions that we plan to address using computational chemistry.

Acknowledgment. We thank Massimo Bietti, Peter Mulder, and a reviewer for helpful remarks about the possible mechanisms of phenoxyl radical formation.

JO061898Z

---

(19) Under standard experimental conditions, radicals could not be detected using either 2-(1-naphthyl)propan-2-ol or 1-naphthyldiphenylmethanol as the aryl carbinol.[14] This is not surprising because naphthyl migrates much more rapidly than phenyl[20] and the 1-naphthoxyl radical has an ESR spectrum showing two equivalent and four non-equivalent hydrogen atoms for a total of 48 lines.[21] It is therefore much more difficult to detect by ESR than the phenoxyl radical which has only 18 lines.

(20) Kharasch, M. S.; Poshkus, A. C.; Fono, A.; Nudenberg, W. *J. Org. Chem.* **1951**, *16*, 1458–1470. Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224–1226.

(21) Dixon, W. T.; Foster, W. E. J.; Murphy, D. *J. Chem. Soc., Perkin Trans.* **1973**, *2*, 2124–2127.

(22) Similarly, the CAN-mediated photooxidation of various alcohols in acetonitrile gave ESR spectra that were interpreted as involving the formation of free alkoxyl radicals as intermediates. For example, with *tert*-butyl alcohol both CH$_3^\bullet$ (from β-scission of Me$_3$CO$^\bullet$) and NCCH$_2^\bullet$ (from H-atom abstraction from the solvent) were observed. See: Grossi, L. *Res. Chem. Intermed.* **1996**, *22*, 315–324.

(23) We thank a reviewer for the suggestions.

(24) Young, L. B.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 5060–5068. Nave, P. M.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1971**, *93*, 4536–4540. Trahanovsky, W. S.; Macaulay, D. B. *J. Org. Chem.* **1978**, *38*, 1497–1499.

(25) Del Giacco, T.; Baciocchi, E.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 5451–5456.

(26) A potential of 2.0 V vs. S. C. E. has been estimated for the NO$_3^\bullet$/NO$_3^-$ couple in acetonitrile,[27] a value that is lower than the oxidation potentials of mono-alkylbenzenes,[28] the oxidation of which by NO$_3^\bullet$ has therefore been interpreted in terms of HAT and PCET mechanisms.[25,27,29]

(27) Baciocchi, E.; Del Giacco, T.; Murgia, S. M.; Sebastiani, G. V. *J. Chem. Soc., Chem. Commun.* **1987**, 1246–1248.

(28) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287–294.

(29) Ito, O.; Akiho, S.; Iino, M. *J. Org. Chem.* **1989**, *54*, 2436–2440.

(30) Grossi and Strazzari[14] suggested that the peroxyl radicals might be formed in this way and also by the trapping of **1**. However, even if **1** are genuine intermediates in these isomerizations, they are certainly too short lived to be trapped by oxygen.

(31) Dixon, W. T.; Moghimi, M.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1713–1720.